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CHEMOELECTRIC ENERGY CONVERSION
FOR NONAQUEOUS RESERVE BATTERIES

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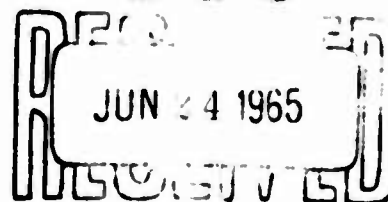
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NAVAL ORDNANCE LABORATORY CORONA
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NAVAL ORDNANCE LABORATORY CORONA

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FOREWORD

This is one of a series of NAVWEPS reports that summarize the quarterly progress in the research on conversion of chemical to electrical energy for application in Navy guided missile auxiliary power supplies. The Electrochemistry Branch, Chemistry Division, is performing this research under WEPTASK RRRE-06-017/211-1/F009-06-05 and R360-FR-104/211-1/R011-01-01. This work is reported to the Interagency Advanced Power Group, Power Information Center on Project Briefs, as PIC 345, PIC 994, and PIC 1011.

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ABSTRACT

A literature search, experimentation, and chronopotentiometry were directed toward an investigation of reference electrodes for use in liq. NH_3 solutions at ambient pressure or to 70 kg/cm.^{2} The problem was defined by experimentation with $Pb/PbCl_2$, as well as with $Tl/TlCl$, In, and Ge. Metals were nitrided for studies in liq. NH_3 during the next quarter. An exhaustive chronopotentiometric survey determined the limiting potentials of acids (ammonium salts that are soluble) in liq. NH_3, using a $Pb/PbCl_2$ reference electrode and a Pt or pyrolytic graphite working electrode. From this data, it is possible to predict why voltaic cells incorporating some of these acids will not operate satisfactorily. Ammonium chloride was the most promising electrolyte in liq. NH_3 and showed a minimum of interfering potentials.

Research hardware cells with the positive halogen compound trichlor-omelamine were tested, and studies of the electrolyte requirement led to the construction and testing of a new type of cell that completely elimi-nated what is normally the electrolyte. In view of the simplicity of con-struction, these latter cells gave promising results.

Ammonia cell exploratory development included satisfactory perform-ance of a transistorized fast-switching test circuit for internal resistance measurements and determination that a $Pb/PbCl_2$ reference electrode did not affect cell performance. Although it had been hoped that intro-duction of $(NH_4)_2SO_4$ close to the anode would precipitate Mg ion and form insoluble $MgSO_4$, thus minimizing the undesirable effect of Mg cations on the cathode, the result was a pronounced adverse effect on internal resistance and performance was lowered. A series of cell tests with Pt, Ag, and stainless steel cathectors showed no significant difference in performance.

An analysis is made of that portion of experimental error attributable to measurement, and the conclusion is that the component of error due to measurement only is less than total experiment variability by an order of magnitude, indicating that recorders of 1 or 2% uncertainty and the general test methods are adequate.

Voltage, power, and energy relations in single-cell performance are evaluated in terms of their relative importance to the intended battery applications, the model FC-2 ammonia battery in particular; and the conclusion is reached that—with respect to power, energy, or voltage efficiency—any one or two may be compromised in some cases to the advantage of the remaining one or two, if there has been an accurate definition of critical parameters for the intended applications. Cell-energy conversion is analyzed in terms of an energy pyramid and by calculations using integral and average methods.

NONAQUEOUS SOLVENT ELECTROCHEMISTRY

by

R. E. Panzer

In the past quarter, emphasis of research was on reference electrodes that can be used in liq. NH_3 solutions either at ambient pressure or in cells pressurized to 70 kg/cm^2 (1000 psi). A literature survey was made of possible reference electrode metals and compounds with regard to solubility, reactivity, and conductivity in liq. NH_3. Investigations with $Pb/PbCl_2$, as well as $Tl/TlCl$, In, and Ge, produced interesting results, and the problem was defined through use of these materials. Preparation of nitrided metals for use in liq. NH_3 was begun after a literature survey and receipt of reprints from R. Juza, of Kiel University, Germany, who is the leading investigator in this field.

An exhaustive chronopotentiometric survey was conducted of acids (ammonium salts) that are soluble in liq. NH_3, to determine the limiting potentials of these materials. From this data, it is possible to predict why voltaic cells incorporating some of these acids will not operate satisfactorily.

Literature Survey of Liquid Ammonia Reference Half Cells

Reference half cells, often called simply reference electrodes, are a most valuable tool of the electrochemist. In the present case, it is necessary that a reference half-cell that is compatible with liq. NH_3 must also be adaptable for use in ambient and pressurized systems, in beaker cells with excess electrolyte, in hardware-type voltaic cells, and in voltammetry studies now being conducted in pressure cells. The pressure parameter has become important because we are now using electrolytes (dissolved in liq. NH_3) that do not reduce the vapor pressure of the solvent as does NaSCN or $LiNO_3$. For this reason, it seemed best to consider only reference electrodes of the second kind, because of the extreme difficulties in preparing electrodes of the first kind in a high pressure system.[1] The latter must have a membrane or other separator between its solution and the cell solution to prevent intermixing of the two solutions. This separator will be a source of an unknown junction potential in the liq. NH_3 systems, as so little is known of the supporting electrochemistry.

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[1] In Ref. 1, the three kinds of electrodes are defined.

The separator would also be subject to high pressure and would have to be rugged. Additionally, four criteria (Ref. 2) must be satisfied by any reference electrode adopted in our investigations. The four criteria are as follows:

1. Reversibility. If current is accidentally passed through the electrode, its potential should return to the original value in a reasonably short time.

2. Reproducibility. Each electrode should have the same potential as others of its kind.

3. Simplicity. Preparation of the electrode should be uncomplicated. Lengthy, exacting preparation and aging are severe limitations to reference electrodes that can be used only once.

4. Stability. Depending on the accuracy of measurements, the potential of an electrode should show an essentially flat curve of potential as a function of time. Further, because cell life is comparatively short, this performance should be achieved immediately on activation of the cell.

Discussion with other researchers in liq. NH_3 electrochemistry indicated that the lead/lead salt systems should be more thoroughly investigated for electrodes of the second kind. Thallium/thallous chloride has been used by Elliot and Yost (Ref. 3) and later by Garner, Green, and Yost (Ref. 4). Because thallous chloride is but slightly soluble in liq. NH_3, this system would be of interest. It must be remembered that a second-kind electrode requires that the electrode be reversible to the anion used (chloride, sulfide, or other). Therefore, one must be able to dissolve in liq. NH_3 a small amount of a salt containing that anion. The chlorides appeared to offer the most promise, and investigations this quarter have centered on them.

Reference Electrode Experimentation

Thallium/thallous chloride electrodes were prepared from small strips of the cleaned metal, which were electrolyzed in dilute HCl soln. to form a heavy coating of the chloride on the metal surface. It was found that, once a coating had formed, the current of the electrolysis dropped; the applied voltage was then increased, the current fall was again noted, and the voltage was again increased. Each time the current fell to zero, the voltage was increased until it was possible to apply 10 volts between the Tl and a Pt cathode with passage of only a few microamperes of current. This same technique was applied to Pb electrodes to give a good coating of $PbCl_2$ on Pb wires or rods as desired. The resulting half cells were then dried thoroughly and placed in the drybox. Preliminary tests were

conducted in the drybox and in cells of the three-compartment type, with the compartments separated by finely fritted glass disks. Solutions used were concentrated $NaSCN$-NH_3 and $LiNO_3$-NH_3; three reference electrodes were immersed and then monitored in pairs to determine potential differences. These potentials were recorded on a Varian G-11 strip-chart recorder from the output of a General Radio Electrometer-Amplifier Type 1230A, which has an input impedance of 10^{14} ohms. As expected, a slight amount of chloride ion was necessary to produce minimum potential differences. However, with Tl, if NH_4Cl is added, the corrosion of the metal by NH_4^+ ion undermines the chloride coating very rapidly and causes excessive drift of the electrode potentials. In neutral solutions, the thallium systems gave only slightly less drift, but potential differences were excessive. Thallium metal has chemical characteristics akin to those of lead (its neighbor on the periodic table), but it is also similar to potassium. It is quite reactive and turns brown when freshly cut, if not protected. It appears that the reactivity of Tl in acidic ammonia solutions eliminates thallium systems from consideration for reference electrode usage. Thallium is also rather toxic and must be handled with gloves, not allowed to contact the skin, nor ingested in any way.

The chloridized lead electrodes were monitored in the same way, and they behaved very well in these cells. Electrodes in NH_3 soln. that was acidified with NH_4Cl showed individual potential differences on the order of 1 to 3 mv for periods up to an hour. Beyond that time, the Pb had been corroded beneath the chloride coating, causing the coating to loosen. The effect of loading the $Pb/PbCl_2$ electrodes by momentarily passing current through them was minimal, as the electrodes returned to their original values within 2 min after this drastic treatment. In a voltaic-cell test, it is doubtful that such a treatment would ever be done deliberately. The effect of adding various amounts of chloride ion and different chlorides (such as lithium, sodium, or ammonium) appeared to be nil, as far as the chloride ion was concerned; once a trace amount was present, further additions had no effect. However, the ammonium ion (the acid ion in liq. NH_3) does erode any exposed Pb surfaces and will in time reduce the effectiveness of the chloride coating. For this reason, the time for using these electrodes is restricted to about 15 min before either potential drift or Pb ion concentration has become excessive. In other types of cells, such as voltaic cells, locating the reference electrode remotely from the working cell electrodes would reduce side effects. The effect of varying the distance (within the cell limitations) between pairs of reference electrodes was found to be very low; the IR drop was much less than the experimental error.

Preliminary experiments were made with In and Ge to process them in some manner so that they would perform well as second-kind electrodes. Little success was attained, and they were never stabilized in liq. NH_3.

Chronopotentiometry in Liquid Ammonia

During this quarter, the Pb/PbCl$_2$ electrode was utilized in pressure cells of the polypropylene type previously described (Ref. 5). The reference electrodes were made of a Pb wire 2 mm in diam. extending through a cell plunger and set in place with epoxy cement. The exposed electrode, about 1 cm long, was coated with PbCl$_2$ by the electrolytic process previously described. Under liq. NH$_3$ pressure of 8.4 kg/cm^2 (120 psig), these electrodes behaved satisfactorily, but had limited lifetimes in the presence of NH$_4^+$ ion (as previously noted). Solutions of many ammonium salts were subjected to electrolysis at constant current between a Pt-wire working electrode and a Pt-disk counter electrode. Alternatively, a pyrolytic graphite (PG) working electrode was fabricated on a plunger end in the cell. A graphite wafer[2] of 2.00-mm diam. was inlaid in the plunger and sealed with epoxy cement. A conductive epoxy material was used to make electrical contact between the back of the graphite disk and an Ni-wire lead. Performance of these salts in voltaic-cell systems can be predicted from the curves resulting from monitoring the potential changes on the working electrode (compared with the reference electrode) by an electrometer and an x-y recorder. The potentials are uncorrected for IR drop between the electrodes, as the spacing between them was only about 3 mm and any correction would be far less than the recording error. The reference electrode was cleaned and renewed for each succeeding series of cell operations, which were conducted rapidly to minimize irreversible changes in the system. Several hundred curves were made during this period, and it would be difficult to present more than a summary of them. Typical curves from NH$_4$Cl are shown in Figure 1, and important voltage plateau levels are listed for various electrolytes in Table 1. The choice of these electrolytes is based on their prospective use in voltaic cell studies by members of this laboratory group.

A number of comments should be made concerning the results of these voltammetric studies. At the outset, it must be understood that the relative duration of the transition times is not particularly significant—although, as usual, they are dependent on the cursity and concentrations of the reacting species. Reagent-grade salts were dried, but no further purification was done. Concentrations were on the order of 5×10^{-3} mole/liter, but only partial dissociation into ionic species occurs, even at these concentrations. A very small break in a curve ofttimes indicates the presence of a trace impurity. The voltage levels observed are reproducible, but it is well known that there is a slight shifting to more negative values with increasing cursity. Over the cursity range of 0.6 to 2.89 ma/cm^2, a shift of 0.05 to 0.09 ma/cm^2 may be observed. There is evidence of a rather high double-layer capacitance when current is reversed from either

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[2]Product of High Temperature Materials, Inc., Boston, Massachusetts.
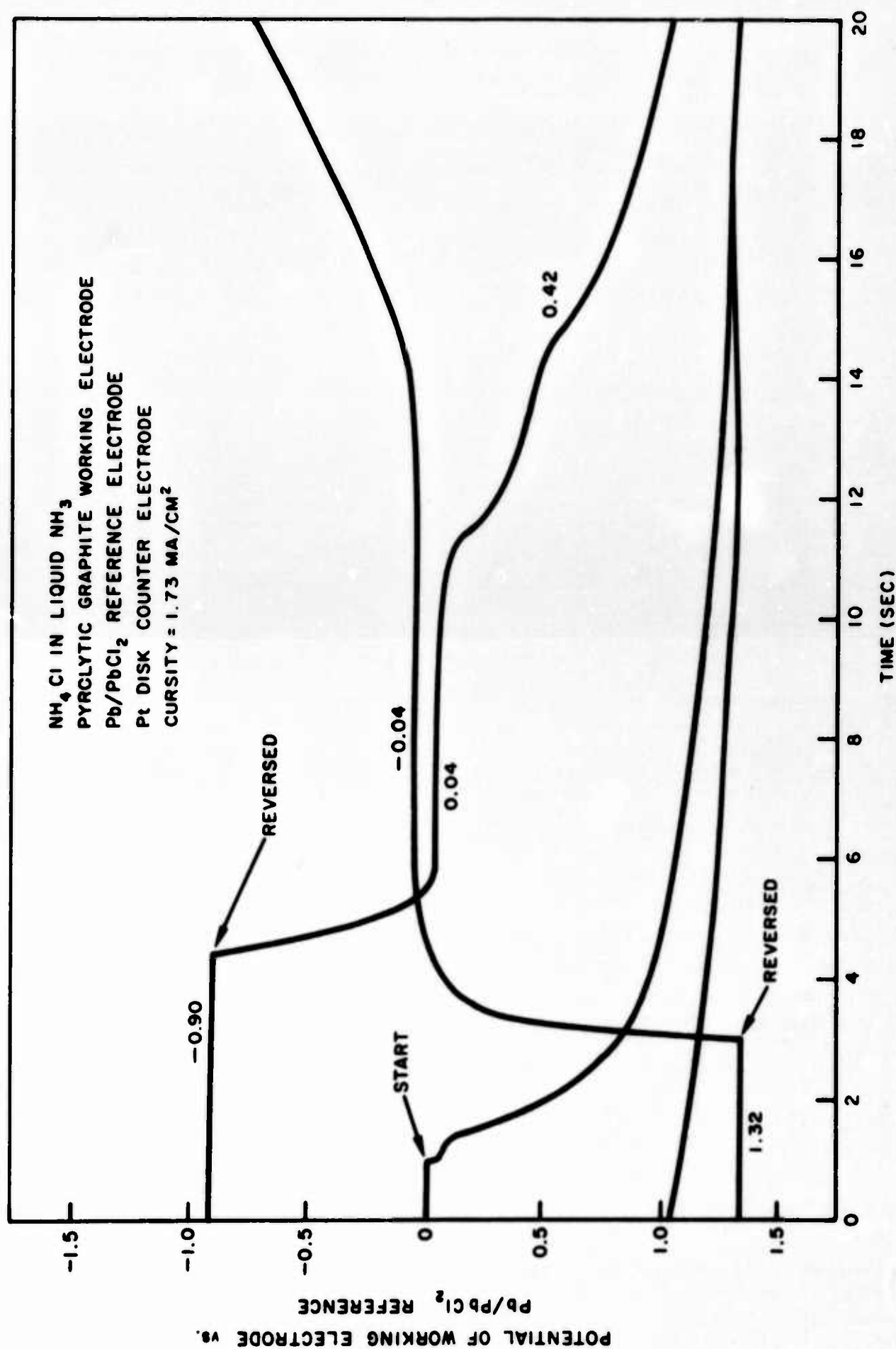
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FIGURE 1. Representative Chronopotentiometric Traces for NH_4Cl

NH_4Cl IN LIQUID NH_3
PYRGLYTIC GRAPHITE WORKING ELECTRODE
$Pb/PbCl_2$ REFERENCE ELECTRODE
Pt DISK COUNTER ELECTRODE
CURSITY = 1.73 MA/CM^2

POTENTIAL OF WORKING ELECTRODE vs.
$Pb/PbCl_2$ REFERENCE

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TABLE 1. Summary of Important Potential Levels for Various
Electrolytes Dissolved in Liquid Ammonia

Electrolyte	Potential Levels (volts)
NH_4F	Small plateau at ±0.09; limiting potentials at -0.22 and +0.30
NH_4Cl	Small plateaus at ±0.10, +0.45 after (-) sweep limiting potentials at -1.00 and +1.40
NH_4Br[*]	Small plateau at +0.08; limiting potentials at -0.08 and +1.17
NH_4I[*]	Limiting potentials at -0.08 and +0.20; no others observed
NH_4ClO_4[**]	Small plateaus at ±0.08, +0.26; limiting potentials at -0.49 and +1.00
$KClO_4$[**]	Small plateaus at ±0.08, -0.42; long plateau at +0.45; limiting potentials at -1.05 and +0.95

[*]NH_4Br and NH_4I display limiting potential at -0.08, which may be due to a highly absorbed species.

[**]Difference between $KClO_4$ and NH_4ClO_4 may be due to dissociation and solubility differences.

(+) or (-); this is shown by the slope of the curve following reversal. Throughout these studies, a series of plateaus or slight breaks occurred at potentials of ±0.04 to ±0.10 volt. If the potential is first started with the working electrode negative, this potential of -0.05 volt may be only a slight break of 1/2 sec duration; the curve then rises to other levels, depending on the electrolyte. On reversing the current from the negative side, the potential then drops to +0.05 ma/cm^2 but maintains this level for as long as 25 sec, depending on the cursity. Kuwana (Ref. 6) has observed a similar potential in cyclic voltammetry and postulates that it is due to absorbed hydrogen on bright Pt, and the anodic curve (where the plateau is much longer) is due to the oxidation of the absorbed hydrogen. In this investigation, his suggestion of pretreating the Pt electrode with cleaning solution has not been followed in time to include the result here. However, it should also be noted that the PG electrode used in these experiments probably would not display such extensive H_2 adsorption. Yet, essentially the same behavior was observed, and in several cases the plateaus were very long at +0.05 volt. The limiting potentials at -1.00 ±0.05 and at +1.30 ±0.05 volts were observed in every solution

where the concentration of the electrolyte was low enough and electrolysis fast enough to deplete the ionic species responsible for potentials less than the limiting potentials. These limiting potentials are believed to be those for the reduction and oxidation of NH_3, since gases forming on the electrodes at relatively high cursities produce an undulating curve. The effect of these limiting potentials in voltaic cells is that any anodic metal with a potential greater than -1.00 volt will reduce the ammonia, and any cathodic material with a potential greater than +1.35 volts will oxidize the ammonia. Thus, gaseous products would be formed at whichever electrode exceeded its respective limiting potential; if both anode and cathode limiting potentials were exceeded, there would be gassing at both electrodes.

A number of important differences were observed in these dilute solutions of ammonium halides, ammonium perchlorate, and potassium perchlorate, as compared with the results of voltammetry in highly concentrated solutions of NaSCN in NH_3. In the highly concentrated solutions, the electrolyte is present at 11 molal concentration (43 wt. %) for $LiNO_3$ and 21 molal (63 wt. %) for NaSCN. These solutions are quite viscous and do not evaporate readily. It is possible that the ammonia is so highly complexed by the dissolved salt that there is actually little or no free liq. NH_3 present to show the limiting potentials observed in the dilute pressurized solutions. A comparable situation arises with 40 wt. % KOH solutions in water, which display characteristics of fused salts, the aqueous portion being drastically subdued in its behavior. This survey leaves no doubt that electrochemistry in the dilute solutions used in pressurized systems is not at all comparable with that in the concentrated solutions named above, and electrochemical results should not be extrapolated from one into the other without due caution.

From the results of this work, the use of NH_4I in voltaic cells would be expected to cause experimental difficulties. At a cathodic potential of -0.45 volt, gassing was observed; on the anodic sweep, a very long plateau observed at +0.20 volt appears to be due to the oxidation of iodide. The ammonium iodide showed high reactivity, and a yellow discoloration was observed in every cell in which NH_4I was used; it would be very reactive with cathodic materials in voltaic cells. There are numerous reasons why ammonium halides and potassium and ammonium perchlorates are not operating satisfactorily in voltaic cells. Also, it is well known in liquid ammonia chemistry that many soluble salts are not greatly dissociated in this solvent because of its low dielectric constant. Previously, observations had revealed a potential of -0.45 volt with a 1 sec transition time in NaSCN (21 molal in liq. NH_3) with added NH_4^+ ion. In the present case, there is a potential level of about -0.49 volt in both the ammonium and the potassium perchlorate dilute solutions. This potential level appears to be due to the reduction of the perchlorate ion; it is reversible, the same potential appearing on the positive sweep. Also observed was

a 20-sec plateau at -0.70 volt. The various negative potentials indicate that perchlorate ion would be readily reduced by active metal anodes in voltaic cells.

In the perchlorate solutions, there is a reversible plateau observed at +0.26 volt. It is only observed if the sweep has been made to the negative side first, indicating that this voltage level is for the reoxidation of some reduced species from perchlorate (chlorate, hypochlorite, etc.). In a series of multiple sweeps, this positive plateau lengthens in a cumulative manner, indicating that the speed of the oxidation is much slower than that of the reduction and that the reduced species accumulates, causing the progressively longer transition times observed. Diffusion of the reduced species out of the immediate region of the double layer would cause a gradual increase in its concentration in the bulk solution with subsequent sweeps.

In a voltaic cell, this reduced species would be produced at the cathode, and (in time, as its concentration increased) would diffuse to the anolyte-anode section, where it could react with the anolyte components or with the active anode metal.

It was found that a minimum cursity of 1.0 ma/cm^2 is required with most electrolytes to deplete the ionic species faster than they are replenished by diffusion to the working electrode from the bulk of the solution. This was shown many times with numerous samples of ammonium chloride, where sharp breaks between potential plateaus were obtained only with cursities greater than 1.45 ma/cm.^{2}

Ammonium chloride appears to be the most promising dilute solution electrolyte with a minimum of interfering potentials between the limiting potentials of -1.05 and +1.40 volts. Whether this prediction will hold true for its use in voltaic cells remains to be seen. Other considerations, such as dissociation and conductivity may limit its usefulness, but they do not affect the results obtained from voltammetry.

Preparation of Nitrided Metals for Electrode Use

Following receipt of various reprints from R. Juza concerning the preparation and properties of nitrides and amides of various metals, work was begun to prepare those which appeared to be of practical use in voltaic and voltammetric studies. Samples of the pure metal in the form of wires or strips were placed in a quartz boat in a tube furnace and exposed to purified nitrogen or ammonia gas while heated to a temperature as determined by the metal in use. The reaction temperature varies widely between metals. In some cases, the tube furnace would not heat the metal high enough, and it was necessary to suspend the metal between wire clips in a reactor vessel and heat the metal by passing a high amperage AC current through the wire. Titanium and nickel were treated in this way.

These preparations are proceeding, and the products will be utilized in electrochemical studies in the next quarter.

Future Work

In the next quarter, the emphasis will be on reference electrodes using the nitrides. An investigation will be made into the possibility of constructing a reference electrode of the first kind in such a manner that it will withstand the high cell pressures now in use. Chronopotentiometric studies with PG and Au working electrodes will be extended to other electrolyte salts, and other types of voltammetry will be considered.

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5. Naval Ordnance Laboratory Corona. Quarterly Report: Chemoelectric Energy Conversion for Nonaqueous Reserve Battery Systems, October-December 1964. Corona, California, NOLC, 15 January 1965. NAVWEPS Report 8229.

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ELECTROREDUCTION OF ORGANIC CATHODE MATERIALS
IN LIQUID AMMONIA SOLUTIONS

by

W. S. Harris

On the basis of new test information, research hardware cell tests were conducted, using the positive halogen compound trichloromelamine (TCM).

Tests were made of a new type of cell construction that eliminated completely what is normally the electrolyte. In view of the simplicity of construction, these cells gave quite promising results.

New Cathode Materials

Data obtained late in the last quarter—in contradiction to that reported (Ref. 1)—indicate that one of the positive halogen compounds, TCM, can be reduced at moderately high efficiencies at a stirred mercury surface in $LiNO_3$ liquid ammoniate.[1]

Because of this later, more accurate data, attempts were made to utilize TCM in cathode structures suitable for high-rate discharge. Research hardware cell tests were made on this material incorporated in a porous carbon cathode. These cells had a lithium anode, and an acid or neutral electrolyte. The results as far as high-rate discharges go have been rather disappointing. When the best one of four similar cells was tested at low rate, it was able to deliver 7 ma/cm^2 at about 1.4 volts for about 5 min. This is very poor when compared with such materials as m-dinitrobenzene (mDNB) and 2,4 dinitroaniline (2,4DNA).

Additional tests were run to determine the effects of additives on high-rate performance. The materials that were considered as battery additives in these tests were compounds that could act as intermediaries in the reduction of the TCM. Using KI as an example, the TCM would oxidize the iodide ion in the bulk of the cathode to iodine, which would then be reduced at the electrochemically active sites. When using mDNB, the intermediaries were envisioned as being its partial reduction products.

If these ideas were successful, full advantage could be taken of the favorable energy density of the TCM as a cathode material, and of the faster electrode kinetics of the reduction of the intermediary.

Experiment 115

The purpose of experiment 115 was to test these ideas about additives as intermediaries in the reduction of TCM. The two additives KI and mDNB were employed in both acid and neutral electrolyte. The cell system was Li anode/electrolyte/TCM pasted-plate cathode. The experimental results indicate that neither additive has a beneficial effect. Contrarily, KI may have a detrimental effect.

The tests at high rate (100 ma/cm^2) were unsuccessful, and the tests at low rate (16 ma/cm^2) were comparable with those of cells without additives.

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[1] These data appeared after Ref. 1 was in publication, and the last entry of the last column in Table 1, page 12 of that report should be changed to read "4.1e/molecule at very low rates."

More basic knowledge of the reaction mechanism and kinetics of TCM reduction is needed before it will be possible to predict methods of utilizing it at high cursities.

Electrolyte Requirements

Studies of the electrolyte requirement for cells were continued as indicated in the last report (Ref. 1). Rather than continue a further reduction in the quantity of electrolyte salts such as NH_4NO_3, NH_4SCN, KSCN, and $NaNO_3$ as started last quarter, it was eliminated entirely. This is not as absurd as it may sound, since mDNB and other specific similar compounds are known to form highly conducting solutions by themselves in liquid ammonia (Ref. 2).

Although troubled by an increased amount of internal shorting (believed due to the absence of salt) the most likely cells showed great promise, considering the simplicity of construction. The cells were constructed with an Li anode, an electrolyte pad consisting of a glass-fiber filter paper inpregnated with only mDNB, and a smooth platiunum cathector. Inherently this type of construction, without a porous cathode, should be capable of producing very thin cells. Since a smooth cathector (such as platinum) is used in this cell, it probably will be operable only for low (10 to 20 ma/cm^2) cursities. High energy density could be obtained by employing very thin cells. At low cursities, Mg may be more desirable than Li. Fabrication of Mg anodes is easier, and no electronic shorting should be encountered.

Future Work

Results of work in this quarter indicated two lines of investigation should be followed in the future as follows:

1. Feasibility study of cells with no soluble salts as electrolytes.

   a. Delineation of the characteristics of thin cells utilizing selected nitro compounds as electrolytes in place of soluble salts.

   b. Adjustment of the system so that Mg anodes may be employed.

   2. A more sophisticated study of the basic electrolyte properties of selected positive halogen compounds, such as trichloromelamine.

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AMMONIA CELL EXPLORATORY DEVELCPMENT

by

J. C. Daley, G. E. McWilliams, and W. C. Spindler

Four experiments were conducted during this quarter in conjunction with five investigations as follows:

1. Incorporation of a reference electrode in hardware-cell tests.

2. Further investigation of the lithium anode and 2,4 dinitroanaline (2,4DNA) oxidant system.

3. Minimizing of the undesirable effect of magnesium cations on the cathode.

4. Refinement of a fast-switching technique for determining internal cell resistance.

5. Continued evaluation of cell materials and fabrication procedures.

Experiment 16

The purpose of 2^3 factorial experiment 16 was to further the understanding of the amalgamated magnesium anode with respect to the construction features presented in Table 1.

Background. Previous work (Ref. 1) indicated that magnesium cations were moving to the cathode and adversely affecting its performance. The new work was to determine if $(NH_4)_2SO_4$ placed close to the anode would act as an "ion precipitant" and form an insoluble precipitate of $MgSO_4$, thereby reducing the undesirable reaction at the cathode.

A conductive cathode matrix of silvered glass fibers (Agfib) was used in this experiment as a substitute for carbon. This material has significantly less electronic resistance than carbon and reduces the smearing that causes intercell leakage paths, which are particularly detrimental in multicell assemblies. The matrix material is produced by the Brashear process used to silver mirrors.

TABLE 1. Treatment Combinations
in Experiment 16

Cell No.	Ion Precip- itant	Cathode Matrix Material	Anolyte Pad Thickness
1	none	carbon	thin
2	used	carbon	thin
3	none	silvered glass fibers	thin
4	used	silvered glass fibers	thin
5	none	carbon	thick
6	used	carbon	thick
7	none	silvered glass fibers	thick
8	used	silvered glass fibers	thick

The thickness of the anolyte pad in working cells has continued to be of questionable significance. It has been postulated that, when very thin pads are used, direct shorting of the cathode to the anode results in lower cell voltage.

In addition to the statistically evaluated factors listed in Table 1, other experimental parameters assessed were as follows:

1. Three recording instruments were used in parallel to determine more accurately the precision of voltage measurements. As the techniques for investigating the performance of working cells improve, it becomes increasingly important to make accurate measurements, so that the small but significant variations in cell operation can be resolved.

2. A transistorized fast-switching circuit was used for internal resistance measurements. The load was removed to measure the internal resistance of the cell during operation; a voltage change from the value prior to noload was frequently observed when the load was reapplied. This noload does not represent a normal battery condition in service operation, and its voltage effect interfers with accurate evaluation of the discharge. To overcome this, a transistorized switching circuit was devised that produces very short but electrically clean switching. The short duration of the noload condition greatly reduces the unwanted effect and still permits the internal resistance measurements to be made. In addition, the circuitry permits the cathode-ray oscilloscope trace of the voltage change to be photographed for study of the polarization phenomena.

3. The compound NH_4Cl was substituted for NH_4SCN, which is normally used as the anolyte salt. This substitution was made to avoid the undesirable reaction that occurs between NH_4SCN and HgI_2. (The HgI_2 is used to amalgamate the Mg anode.)

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4. The cathode pads were fabricated with a modified Büchner-funnel device that resembles a paper maker's sheet mold. Freon was used as a vehicle. The chemical constituents are not soluble in Freon, and the slurries were prepared in a high-speed blender to ensure homogeneity.

Cell Construction. The construction details of these 1-cm^2 cells are shown in Figure 1. The thickness measurements for the two variations are taken under relatively light pressures and do not represent the true thicknesses of compressible components in a battery environment. This measurement is easily made with a micrometer and is useful for initial evaluations.
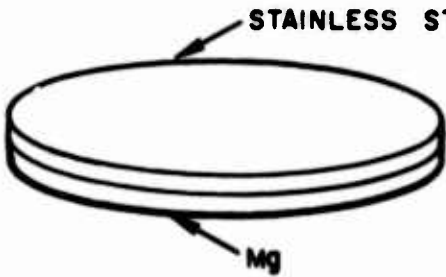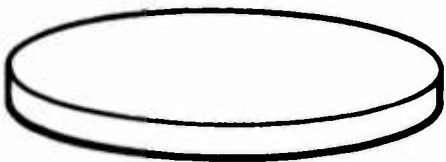
Test Conditions. The test conditions were as follows:

1. Test fixture: single-cell test fixture, Mod. 1 (Ref. 2)

2. Temperature: 24°C

3. NH$_3$ activation pressure: 60 atm

4. Circuit resistance: 20.8 ohms

5. Noload pulses: 1 ms duration, applied at 15 sec.
   1, 2, 3, 5 min

6. Test circuit: schematic shown in Figure 2

7. Assembly pressure: 59 kg/cm^2

Cell Internal Resistance. The oscilloscope traces of the fast noload switching indicate the IR drop of the cells ranged from 0.1 to 0.2 volt and cell resistance ranged from about 1 to 3 ohms. An example of the traces is shown in Figure 3. Analysis of the data shows that the causes of cell-voltage decline is almost entirely nonohmic. As indicated in Figure 2, the downward deflection of the trace is in reality an increase in cell voltage.

Conclusions. Results of experiment 16 are summarized in Figure 4 and led to the following conclusions:

1. None of the cells performed well enough to be considered for present high-current applications.

2. Factorial analysis indicates that interaction AB and factor C were significant above 97.5% at V10 (voltage after 1.0 min). Inspection of the AB interaction shows the significance to be a low value at Low A

14

COMPONENT	WEIGHT (MG/CM^2)	THICKNESS[a] (MM)
STAINLESS STEEL		
BIMETAL[b]		
Mg EVAPORATED ON STAIN-LESS STEEL ANECTOR		
Mg	10.4	0.08
STAINLESS STEEL	21.4	0.03
TOTAL	31.8	0.11
ANOLYTE PAD (SINGLE)		
GLASS FILTER PAPER[c]	9.0	
KI	10.0	
HgI_2	3.0	
$(NH_4)_2 SO_4$ (WHEN USED)	15.0	
TOTAL PAD THICKNESS		0.48
CATHODE PADS		
2,4 DNA	5.7 ⎫	
NH_4Cl	20.0 ⎬	0.89
Agfib (WHEN USED)	17.2 ⎭	
CARBON AND GLASS FIBERS (WHEN USED)		
CARBON	11.6 ⎫	0.70
GLASS	5.7 ⎭	
CATHECTOR		
STAINLESS STEEL ANVIL		
TOTAL THICKNESS OF CELL (SINGLE ANOLYTE PAD)		
Agfib MATRIX CELL		1.48
CARBON MATRIX CELL		1.29

[a] MEASURED WITH MICROMETER UNDER RELATIVELY LIGHT PRESSURE.
[b] BIMETAL FROM CATALYST RESEARCH CORP.
[c] FROM CARL SCHEICHER AND SCHUELL CO.

FIGURE 1. Cell Construction for Experiment 16
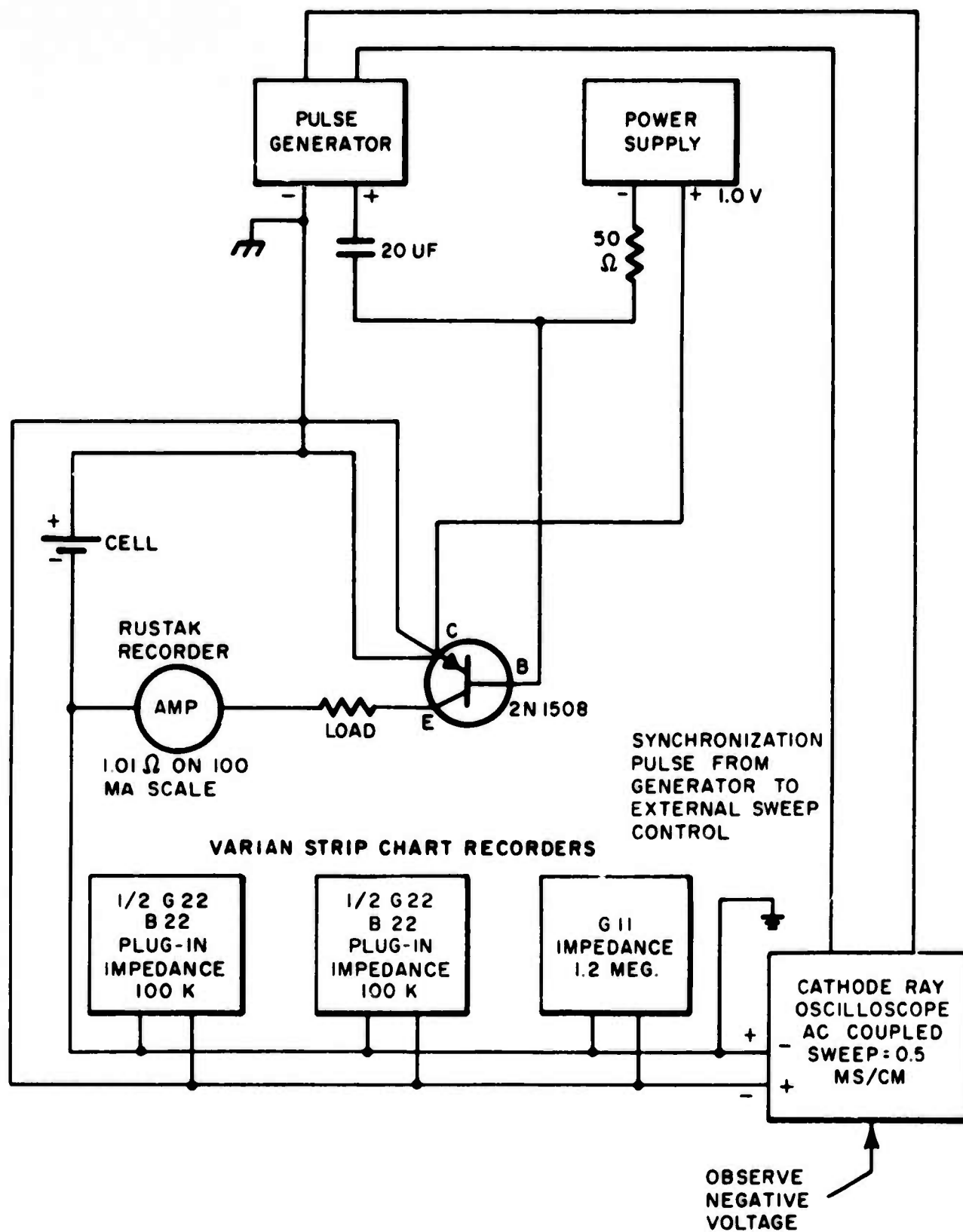
FIGURE 2. Cell-Test Circuit for Experiment 16

16

0.5 MS/DIVISION
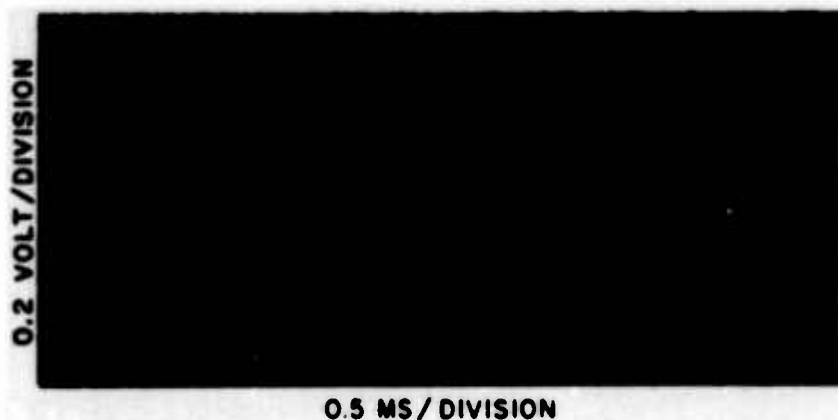
FIGURE 3.   Typical Fast-Switching Noload Pulse

High B, which is no ion precipitant with Agfib. Factor C, anolyte thickness, appears to produce slightly lower voltages when two pads are used. The lack of similar indications at other times during discharge minimizes the importance of the AB interaction and factor C.

3.   The cells with Agfib have an unusually shaped discharge curve (Figure 5) during the first minute. This shape indicates that at first the Agfib cells have higher voltages than cells using carbon, but after about 1 min this advantage disappears.

4.   In general, no information of immediate importance to hardware design evolved from this experiment. However, the fast-switching technique shows good promise of becoming an important method of investigation.

5.   The data for analysis of measurement precision are discussed in the section of this report on Analysis and Evaluation of Experiments.

Experiment 17

Two pilot tests were conducted to determine the performance of the $Li/NaNO_3/2,4DNA-NH_4NO_3-C/$stainless steel system with and without the $(NH_4)_2SO_4$ ion precipitant in the anolyte pad as used in experiment 16. All test parameters were the same as in experiment 16, except as shown in Figure 6.

Cell Construction.   The details of cell construction are shown in Figure 6. Several important parameters of this construction are as follows:

1.   The glass fiber retaining ring (necessary to prevent shorting to the cathector) surrounds the bimetal, resulting in a smaller active anode area. It is felt that the cursity of the cell should be calculated using the cathode area, ignoring the reduction in anode area at the present time.

FACTORIAL PLAN AND CELL PERFORMANCE SUMMARY EXPERIMENT 16

SINGLE CELLS DISCHARGED AT FIXED LOAD 20.8 OHMS

FACTORS AND LEVELS	AVERAGE VOLTAGES AT SELECTED TIMES				
	PEAK	4 SEC	1.0 MIN	3.0 MIN	5.0 MIN
A. ION PRECIPITANT					
LO. NONE	1.57	1.38	1.03	0.77	0.53
HI. WITH	1.43	1.25	1.08	0.83	0.62
B. CATHODE MATRIX					
LO. CARBON	1.48	1.19	1.07	0.79	0.55
HI. AG GLASS	1.52	1.45	1.04	0.81	0.61
C. ANOLYTE THICKNESS					
LO. THIN	1.59	1.39	1.11	0.85	0.59
HI. THICK	1.41	1.25	1.00[a]	0.75	0.56
AB INTERACTION					
HI B LO A (WORST)	1.46	1.43	0.96[a]	0.77	0.56
RANGE MIN	1.19	1.01	0.88	0.67	0.39
RANGE MAX	1.73	1.67	1.19	0.91	0.71
STANDARD DEVIATION [b]	0.18	0.18	0.01	0.03	0.14

[a] Denotes the unfavorable level that is significant above 98% by the F test.

[b] Square root of the estimate of error variance; three degrees of freedom from the interactions.

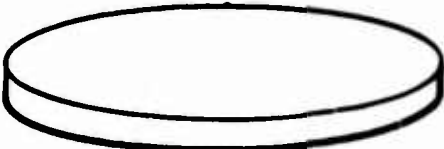FIGURE 4. Machine Printout of Experiment-16 Cell-Performance Summary
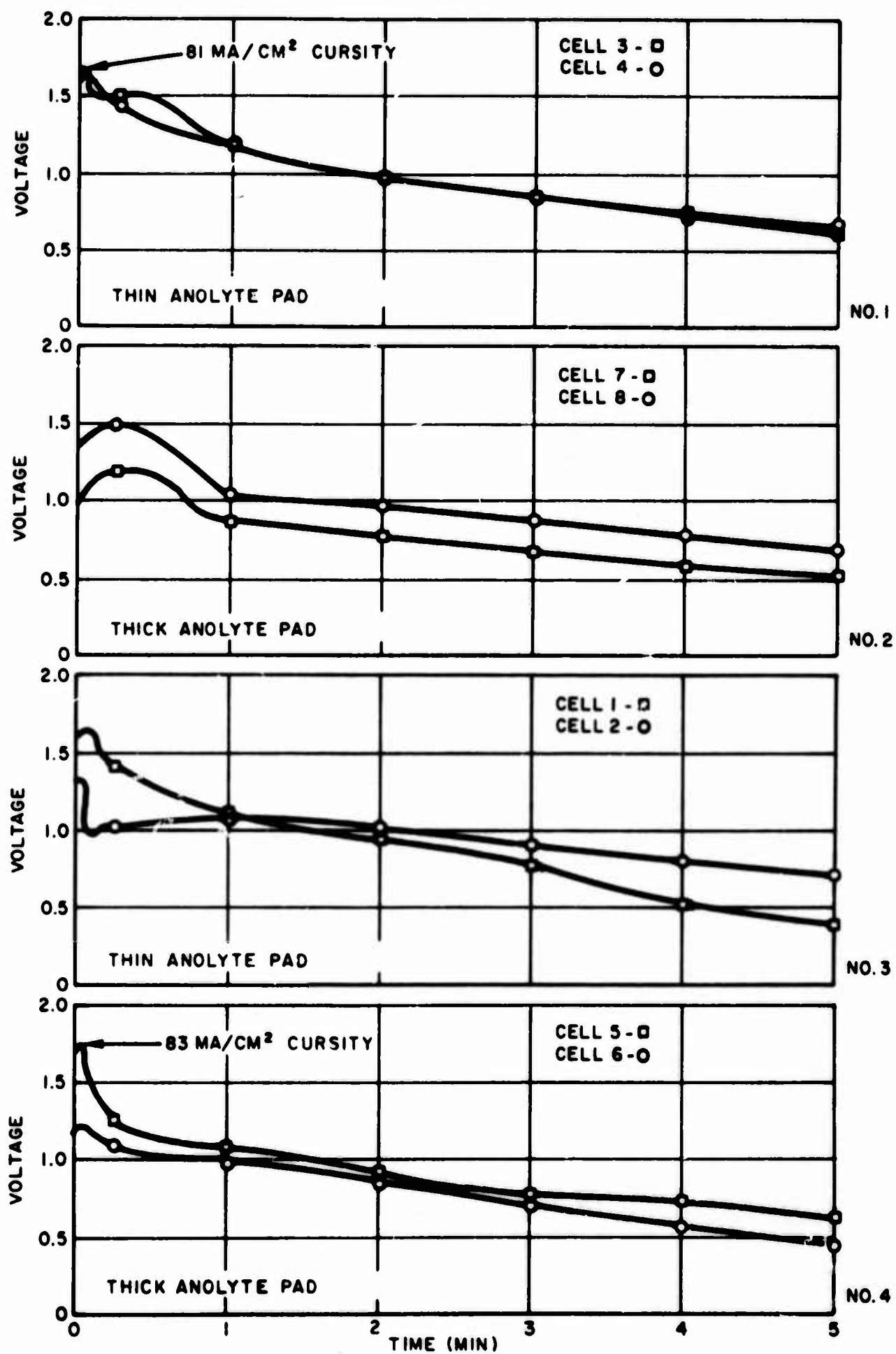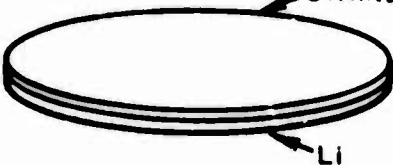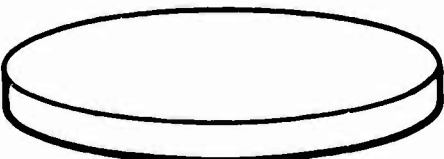
FIGURE 5. Experiment-16 Discharge Summary
(20.8-Ohm Constant Load)

19

COMPONENT	WEIGHT (MG/CM^2)	THICKNESS[a] (MM)
STAINLESS STEEL		
BIMETAL		
Li PRESSED ON STAINLESS STEEL ANECTOR		
Li	34.6	0.62
STAINLESS STEEL	244.5	0.31
TOTAL	279.1	0.93
RETAINING RING		
GLASS FILTER PAPER	1.0	0.48
ANOLYTE PAD		0.48
GLASS FILTER PAPER	9.0	
NaNO$_3$	15.0	
(NH$_4$)$_2$ SO$_4$ (WHEN USED)	20.0	
CATHODE PAD		0 70
NH$_4$ NO$_3$	38.4	
2,4DNA	7.5	
CARBON AND GLASS FIBERS		
CARBON	14.7	
GLASS FIBERS	5.7	
CATHECTOR		
STAINLESS STEEL ANVIL		
TOTAL THICKNESS OF CELL[a]		1.83

[a] THICKNESS OF STAINLESS STEEL ANECTOR ADJUSTED TO THE SAME THICKNESS AS THAT OF A Mg CELL.

FIGURE 6. Cell Construction for Experiment 17

Therefore, the cursities reported for Li cells are based on the 1-cm^2 cath de area, even though the area of the Li anode is 0.713 cm^2.

2. The 0.31-mm-thick stainless steel anector does not represent a construction that would be used in a battery. This material is used only for convenience in the cell test fixture.

3. The thicknesses shown for the "soft" components are measured under lighter compression than that present in battery construction, and they represent upper dimensional limits when used for battery-design calculations. The cell under battery compression conditions would measure approximately one-half to three-fourths the indicated thicknesses.

<u>Test Results and Conclusions.</u> The cell containing the $(NH_4)_2SO_4$ clearly operated below the level of the cell not containing this "ion precipitant." The discharge curves of Figure 7 clearly illustrate this fact. The presence of the $(NH_4)_2SO_4$ has a pronounced effect on the internal resistance of the cell as shown in Table 2. The use of an ion precipitant lowers cell performance in this geometry.
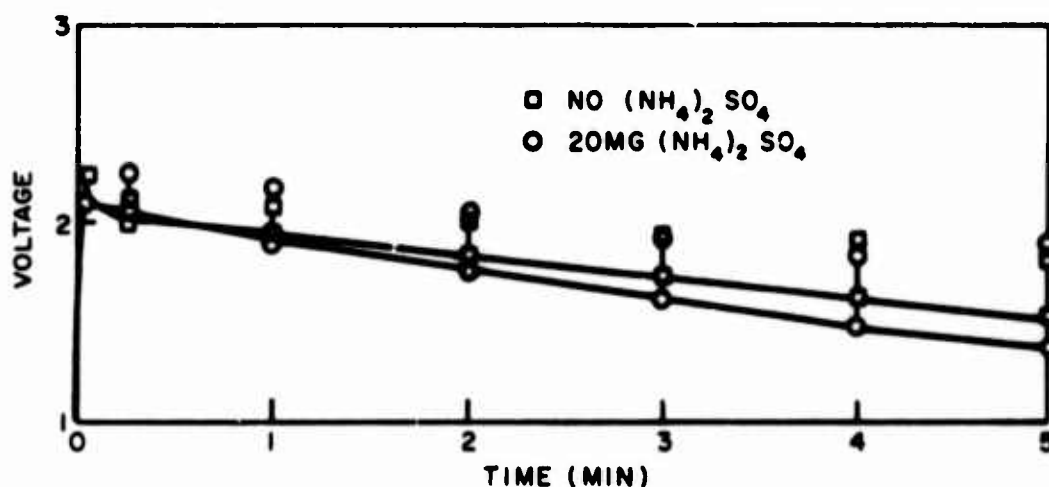

FIGURE 7. Experiment-17 Discharge Summary
(20.8-Ohm Constant Load)

Experiment 18

This experiment was intended to be analyzed as a 2^3 factorial, but (due to erratic cell performance at one level) it was not feasible to use the statistical form of analysis.

TABLE 2. Effect of Ammonium Sulfate on Cell Performance

Variable	Cell voltage at 20.8-ohm load resistance						
	PLV[a]	15 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
Without $(NH_4)_2SO_4$	2.24	2.04	1.95	1.85	1.74	1.63	1.54
With $(NH_4)_2SO_4$	2.11	2.05	1.92	1.78	1.62	1.48	1.39
	Internal Resistance (ohms)						
Without $(NH_4)_2SO_4$		0.8	1.4	2.0	2.6	3.3	3.7
With $(NH_4)_2SO_4$		2.0	2.6	3.0	4.2	5.2	7.3

[a] Peak load voltage.

Background.   The use of a reference electrode has long been a recognized means of obtaining much detailed information from electrochemical cells. Figure 8 shows a reference electrode consisting of a $Pb/PbCl_2$ electrode[1] formed by electrolyzing the Pb in a dilute HCl solution. Electrolytic connection to the cathode pad surface is provided by a salt bridge. This experiment was designed primarily to determine the effect of the presence of the reference electrode on cell performance.

Current hardware studies by Harris[2] with similar Li cells indicated an initial peak noload voltage of 2.8 volts per cell. Experiment 18 was an attempt to verify that performance.

Cell Construction.   The construction details of the Mg and Li cells are shown in Figures 9 and 10, respectively. It must be noted that the weight and thickness of the Li cell anector has been adjusted in calculating total cell thicknesses for comparison purposes. Available material determined the Li anector thickness. However, the Li could have been pressed on an anector as thin as that used in the Mg cell. The amount of 2,4DNA is calculated on the basis of a 65% efficiency for a 12-electron reaction. The amounts of NH_4SCN and NH_4NO_3 in the Cathode pad are stoichiometric ratios with the oxidant.

---

[1] Developed by R. E. Panzer, NOLC.

[2] Discharge characteristics under load for cells 825, 826, 827, 829, and 830 were mentioned in Ref. 3, but noload performance has not been published.

ANVIL STAINLESS STEEL
POSITIVE CONNECTION

REFERENCE
ELECTRODE
CONNECTION

EPOXY INSULATION
(MIRACLE 428)

O-RING

SALT BRIDGE

POLYPROPYLENE
SLEEVE

STAINLESS STEEL
CAP

RETAINING RING

POLYPROPYLENE
INSULATING CAP

$Pb/PbCl_2$

CATHODE PAD

ANOLYTE PAD

LI ON STAINLESS
STEEL

ANVIL STAINLESS
STEEL

O-RING

NEGATIVE CONNECTION

NOTE:
CELL WITHOUT REFERENCE
ELECTRODE HAS PLAIN
STAINLESS STEEL UPPER
ANVIL.

FIGURE 8. Reference Electrode in Typical Test-Cell
Structure

23
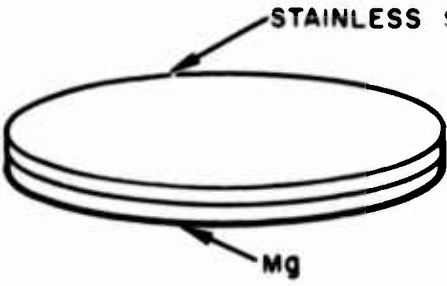
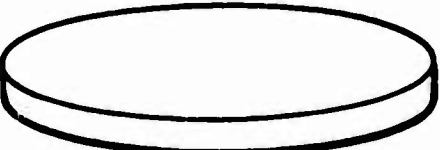| COMPONENT	WEIGHT (MG/CM^2)	THICKNESS (MM)
STAINLESS STEEL		
BIMETAL		
Mg EVAPORATED ON STAIN-		
LESS STEEL ANECTOR		
Mg	10.4	0.08
STAINLESS STEEL	21.4	0.03
TOTAL	31.8	0.11
ANOLYTE PAD		
GLASS FILTER PAPER	9.0	
NH$_4$SCN	36.3	
TOTAL PAD THICKNESS		0.45
CATHODE PAD		
Agfib	17.1	
NH$_4$SCN	36.3	
2,4DNA	7.3	
TOTAL	60.7	0.89
CATHECTOR		
STAINLESS STEEL ANVIL		
TOTAL FOR CELL	137.8	1.45

FIGURE 9. Mg-Cell Construction for Experiment 18

COMPONENT	WEIGHT (MG/CM^2)	THICKNESS (MM)

STAINLESS STEEL

BIMETAL
Li PRESSED ON STAINLESS
STEEL ANECTOR

	WEIGHT	THICKNESS
Li	34.6	0.62
STAINLESS STEEL	244.5	0.31
TOTAL	279.1	0.93

RETAINING RING
GLASS FILTER PAPER   1.0   0.48

ANOLYTE PAD
GLASS FILTER PAPER	9.0	
NH_4NO_3	15.0	
TOTAL	24.0	0.48

CATHODE PAD
Agfib	17.1	
NH_4NO_3	38.4	
2,4DNA	7.4	
TOTAL	62.9	0.89

CATHECTOR
STAINLESS STEEL ANVIL

TOTAL FOR CELL   143.9   2.02

FIGURE 10. Li-Cell Construction for Experiment 18

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Li Anode Preparation. The anode assemblies are produced by pressing a small piece of Li metal against the roughened stainless-steel surface of the anector in a conventional die. The active metal is kept under oil until just prior to pressing, when it is quickly rinsed in solvent and placed in the die. A disc of oil-covered mylar is placed over the assembly, the die is closea, and a load of 900 to 2000 kg is applied to the 0.71-cm^2 area. The resulting assembly is stored in oil until needed.

Test Conditions. The conditions for the cell testing were as follows:

1. Test fixture: single-cell test fixture, Mod. 1

2. Temperature: 24°C

3. Activation pressure: 60 atm

4. Circuit resistance: see discharge curves, Figure 11

5. Assembly pressure: 59 kg/cm^2

6. Oscilloscope monitoring: first 5 sec of performance

The cells were tested in random order, and the output was monitored on Varian strip-chart recorders. The circuit shown in Figure 12 was devised to switch the reference-electrode recorder back and forth between cathode and anode, utilizing the single amplifier available.

Test Results. Figure 11 summarizes the results of using the treatment combinations in Table 3.

TABLE 3. Treatment Combinations
in Experiment 18

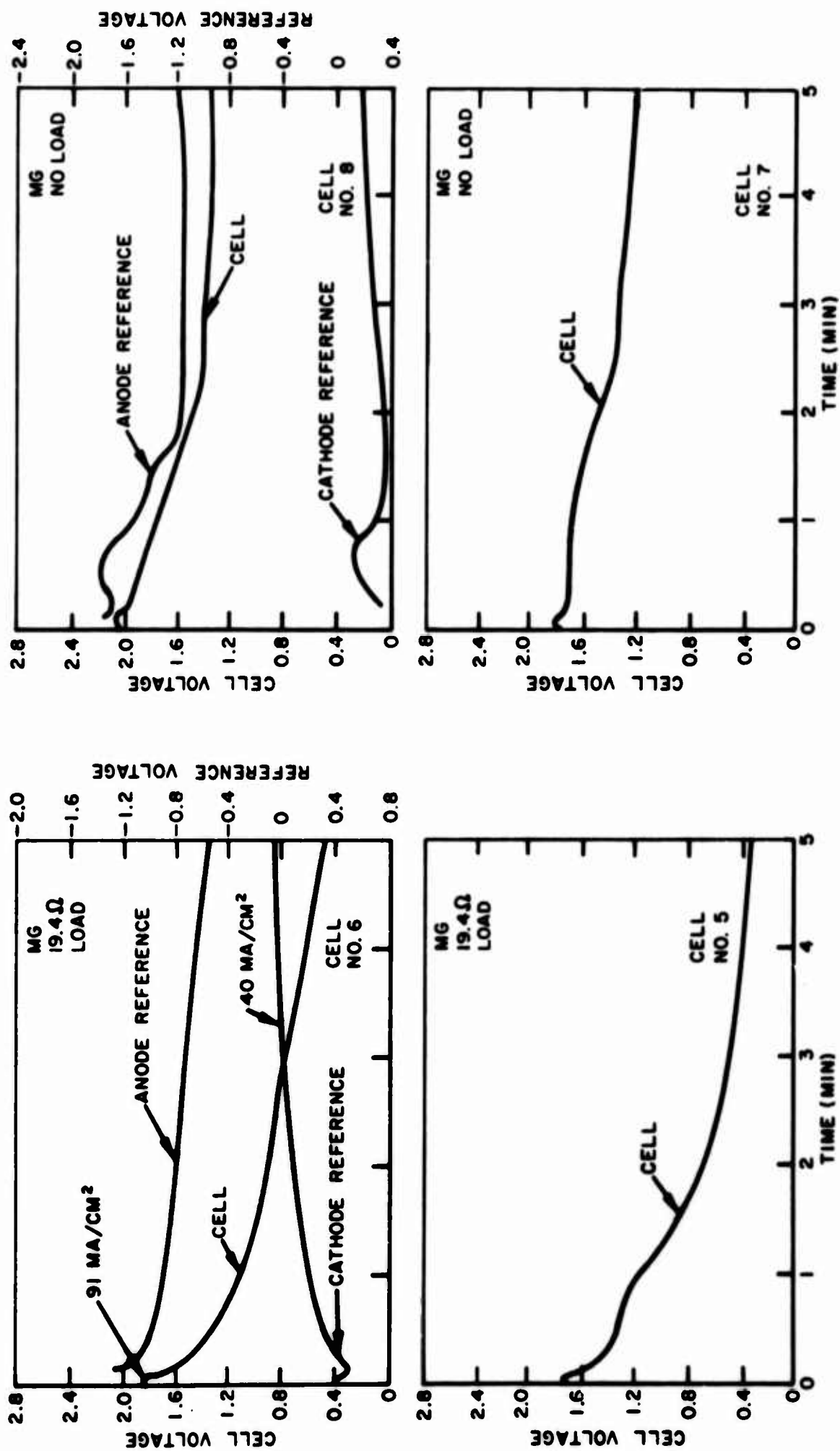| Cell No.	Reference Electrode	Load Resistance	Anode Material
1	none	load	lithium
2	used	load	lithium
3	none	noload	lithium
4	used	noload	lithium
5	none	load	magnesium
6	used	load	magnesium
7	none	noload	magnesium
8	used	noload	magnesium

FIGURE 11. Experiment-18 Discharge Summary (Various Loads as Noted)
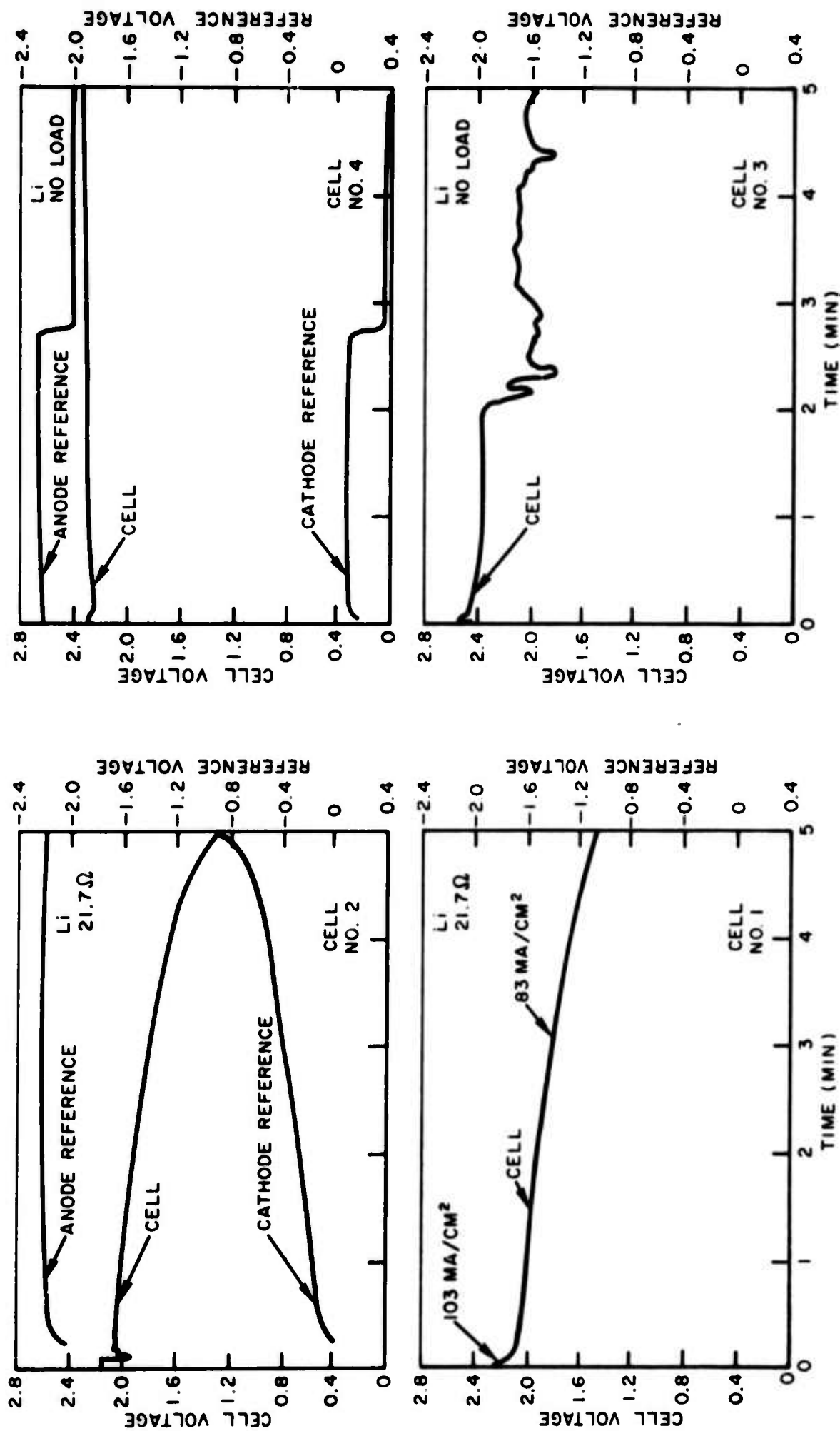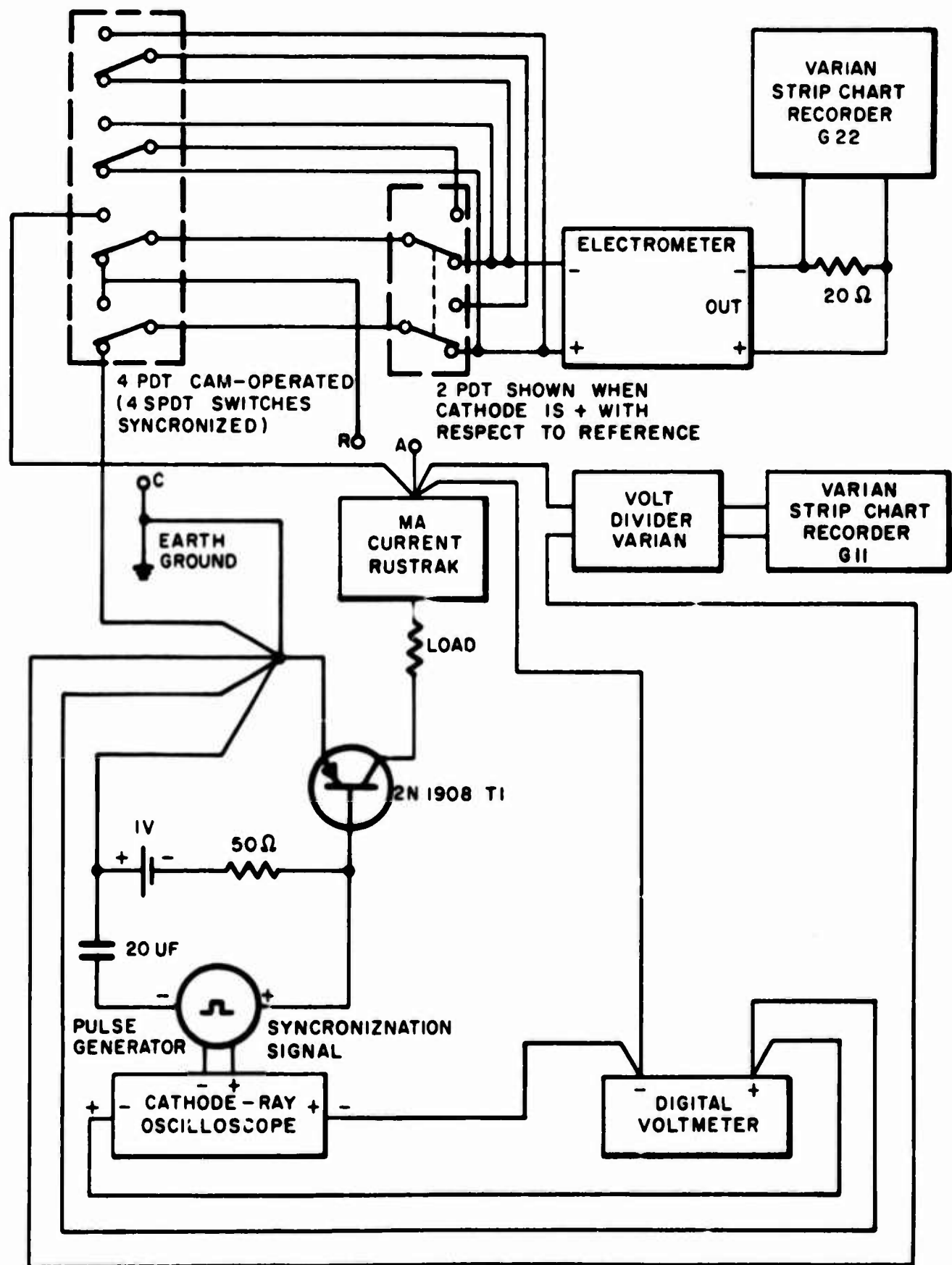
27

FIGURE 11. (Contd.)

28

FIGURE 12. Cell Test Circuit for Experiment 18

29

<u>Conclusions.</u> Results of experiment 18 led to the following conclusions:

1. Comparison of the discharge curves in Figure 11 and examination of the cell discharge data shown in Table 4 indicate the presence of the reference electrode in the cell construction did not measurably affect the cell performance.

2. The shorting condition in the Li noload test (cell 3) was experienced on four successive tests. The cell containing the reference electrode did not short. This performance suggests (1) the conductive lithium blue (formed when liquid NH_3 reaches the Li anode) provides shorting paths through the anolyte pad interstices to the cathode, and (2) these paths are destroyed during load tests, thereby eliminating the shorting condition. It further appears that the presence of a reference electrode also inhibits the formation of these shorting paths. Further tests are needed to verify these postulations.

3. The voltages produced in both load and noload tests were lower than those measured by Harris (Ref. 3). A careful comparison of the two experimental approaches is being conducted to ascertain the reasons for the disagreement.

4. The Li cell potential is 0.4 volt higher than that of the Mg cell at 100 ma/cm^2 cursity. The Mg cell has a 72% decay in 5 min, compared with 35% for the Li cell.

5. Figure 13 illustrates the marked differences in activation characteristics between the two cells. The Li cell activates approximately twice as fast as the Mg cell.

Experiment 19

Experiment 19 was designed as a 3×3 Latin square experiment (Figure 14) and was conducted primarily to learn more about the role of the cathector material in cell performance. Coupled with this objective was the study of the effects of variations in anode materials and three different electronic loading conditions.

<u>Background.</u> As pointed out in the conclusions on experiment 18, of this report, a difference exists between peak noload voltages of Li anode cells tested by Harris and hardware cells tested in the Mod. 1 cell-test fixture (Ref. 2). It was postulated that the cathector material could account for a significant portion of this large voltage difference. Harris' cells contained a Pt cathector as compared to stainless steel for the Mod. 1 fixture hardware cells. To broaden the scope of the experiment, Ag cathectors were also evaluated.

TABLE 4. Experiment-18 Cell-Performance Summary

Cell		Circuit	Reference	Cell Voltage at Selected Times						
Type	No.	Resistance	Electrode	Peak	15 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
Li peak current = 100 ma/cm²	2	load	used	2.15	2.06	2.01	1.94	1.84	1.66	1.31
	1	load	not used	2.25	2.09	2.01	1.95	1.81	1.68	1.47
	av. 1&2			2.20	2.07	2.01	1.94	1.82	1.67	1.39
	4	noload	used	2.32	2.28	2.32	2.31	2.31	2.32	2.32
	3	noload	not used	--	--	--	--	--	--	--
Mg peak current = 90 ma/cm²	6	load	used	1.86	1.53	1.11	0.90	0.77	0.62	0.49
	5	load	not used	1.76	1.43	1.16	0.70	0.51	0.40	0.34
	av. 5&6			1.80	1.48	1.14	0.80	0.64	0.51	0.41
	8	noload	used	2.07	1.96	1.78	1.50	1.41	1.36	1.37
	7	noload	not used	1.84	1.74	1.70	1.51	1.36	1.28	1.24
	av. 7&8			1.95	1.85	1.74	1.51	1.39	1.32	1.31
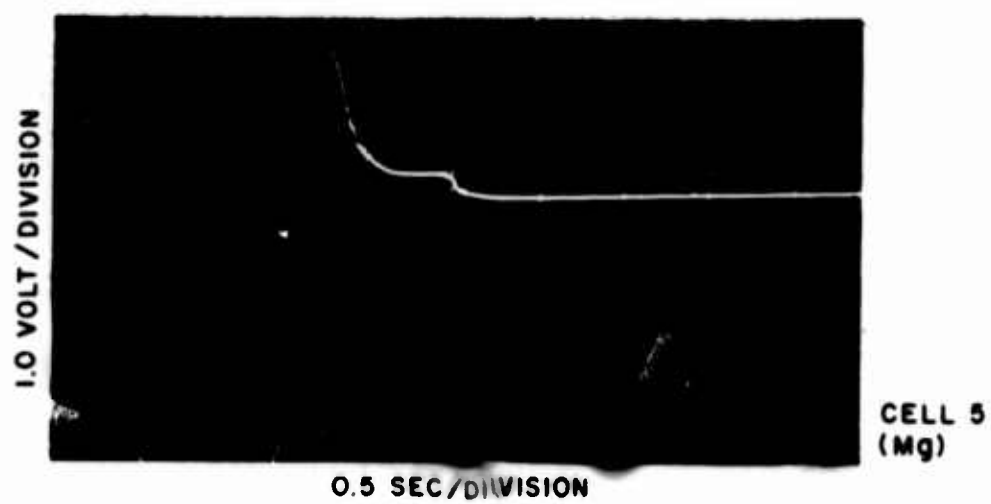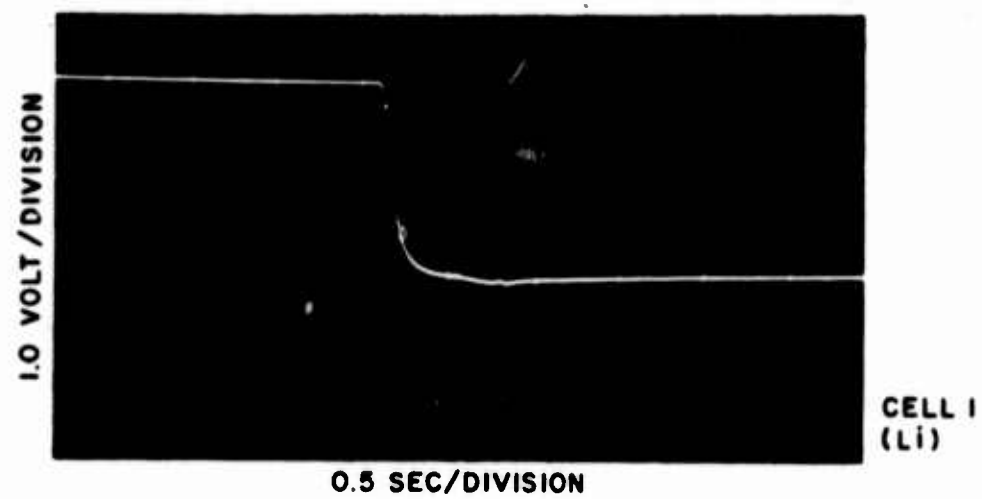
FIGURE 13. Voltage Rise at Activation
in Experiment 18

CATHECTOR

	Stainless Steel	Ag	Pt
Li	Light Load	Medium Load	Noload
Rolled Mg	Noload	Light Load	Medium Load
Sheet Mg	Medium Load	Noload	Light Load

ANODE

FIGURE 14.   Experiment 19—3 × 3 Latin Square Test Plan

Most of the Mod. 1 cell studies have been conducted with a bimetal composed of evaporated magnesium on a stainless-steel anector.[3] Some cell studies have been made using Mg-stainless-steel bimetal produced by a rolling process.[4] In this experiment, the rolled material was compared with a commercially available pure Mg sheet.[5] The Li anodes used were made by the process previously described in this report for experiment 18.

Cell Construction.   The construction details of the Li and Mg cells are shown in Figures 15 and 16, respectively.

Two additional single cells (test cells 10 and 11) were constructed by the pasted-cathode method, and these were tested outside of the Latin-square matrix.   These cells were run to evaluate the effect of pasted-plate construction on cell performance.   The cathode matrix is formed by mixing the ingredients with sufficient water to form a thick paste and

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[3] Product of Catalyst Research Corp., Baltimore, Maryland.

[4] Product of Metals and Controls, Inc., Attleboro, Massachusetts.

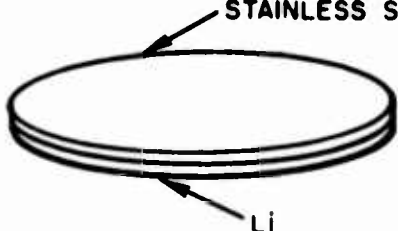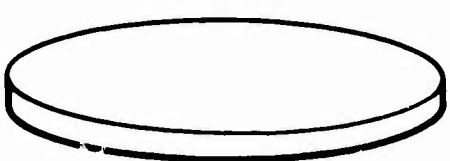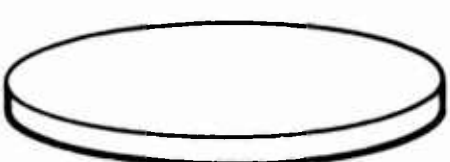[5] BT 92-56, manufactured by Dow Chemical Co., Midland, Michigan.
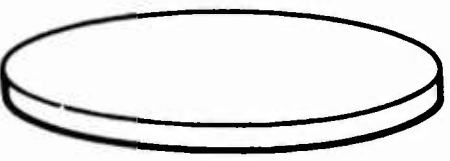
COMPONENT	WEIGHT (MG/CM^2)	THICKNESS (MM)
STAINLESS STEEL		
BIMETAL		
Li PRESSED ON STAINLESS		
STEEL ANECTOR		
Li	34.6	0.62
STAINLESS STEEL	244.5	0.31
TOTAL	279.1	0.93
RETAINING RING		
GLASS FILTER PAPER	1.0	0.48
ANOLYTE PAD		
GLASS FILTER PAPER	9.0	
NH$_4$ NO$_3$	15.0	
TOTAL	24.0	0.48
CATHODE PAD		
Agfib	17.1	
NH$_4$ NO$_3$	38.4	
2,4DNA	7.4	
TOTAL	62.9	0.89
CATHECTOR - VARIABLE		
TOTAL CELL (ADJUSTED AS NOTED IN TEXT)	143.9	2.02

FIGURE 15. Li-Cell Construction for Experiment 19
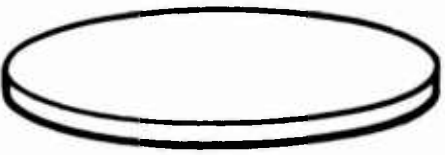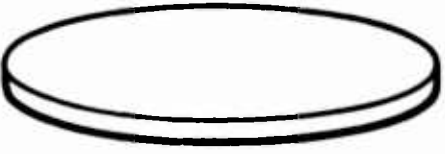
COMPONENT	WEIGHT (MG/CM^2)	THICKNESS (MM)
ROLLED BIMETAL		
Mg	22.5	0.10
Ag	27.8	0.05
TOTAL	50.3	0.15
SHEET Mg (LAMINATED TO STAIN-LESS STEEL ANECTOR WITH CONDUCTIVE EPOXY)	73.3	0.42
ANOLYTE PAD		
GLASS FILTER PAPER	9.0	
NH_4 SCN	36.3	
TOTAL	45.3	0.45
CATHODE PAD		
Agfib	17.1	
NH_4SCN	36.3	
2, 4DNA	7.3	
TOTAL	60.7	0.89
CATHECTOR - VARIABLE		
TOTAL FOR CELL ROLLED	156.3	1.49
SHEET (ADDING WEIGHT AND THICKNESS OF Ag)	207.1	1.81

FIGURE 16. Construction of Rolled-Mg Bimetal and Sheet-Mg Cells for Experiment 19

spreading the mix into a cavity that contains the cathector. The system was

$$Li/NH_4NO_3/2,4DNA-NH_4NO_3-C/Ag, \text{ stainless steel, or Pt}$$

The resulting pads were 0.66 mm thick and contained 94 and 86 mg of mix, respectively. The mix contained

12.1 wt. % of 2,4DNA

24.3 wt. % carbon (5:1 graphite to acetylene black)

63.6 wt. % NH_4NO_3

Test Conditions. The test conditions were identical with those of experiment 18.

Test Results. Results of experiment 19 are summarized in Table 5. Examination of the recorder traces for the cells of this experiment indicated that data in the nine tests of the Latin square could not be statistically analyzed because of erratic voltages. The fluctuations were reflected on the anode-reference trace, indicating the cause of the fluctuations to be associated with the anode. These fluctuations were not present in the two pasted-cathode noload tests. The chart records shown in Figure 17 illustrate discharge characteristics of the pasted-cathode cells with the reference electrode traces superimposed on the total cell voltage. The voltage of the cells, prior to activation, could not be reduced by applying a vacuum in the same way that was used for the other nine cells of the experiment. On activation, the cell voltage actually lowered. The reason for this has not been discovered. A defective relay caused the reference-electrode reading prior to 15 sec to be lost. The effect of applying a 41-ohm load resistance can be observed at 5 min.

Cells activated under load activate more slowly than those activated on open circuit. Some Li cells activated under a noload condition have a spike of 0.2 to 0.3 volt at the initial rise. Load tests do not have this.

Examination of the activation photos in Figure 18 show that all tests exhibited a small irregularity in the voltage trace at times from 0.5 to 1.75 sec after activation. The Mg anode cells produced the step voltage rise that is sometimes observed in NH_3 battery tests.
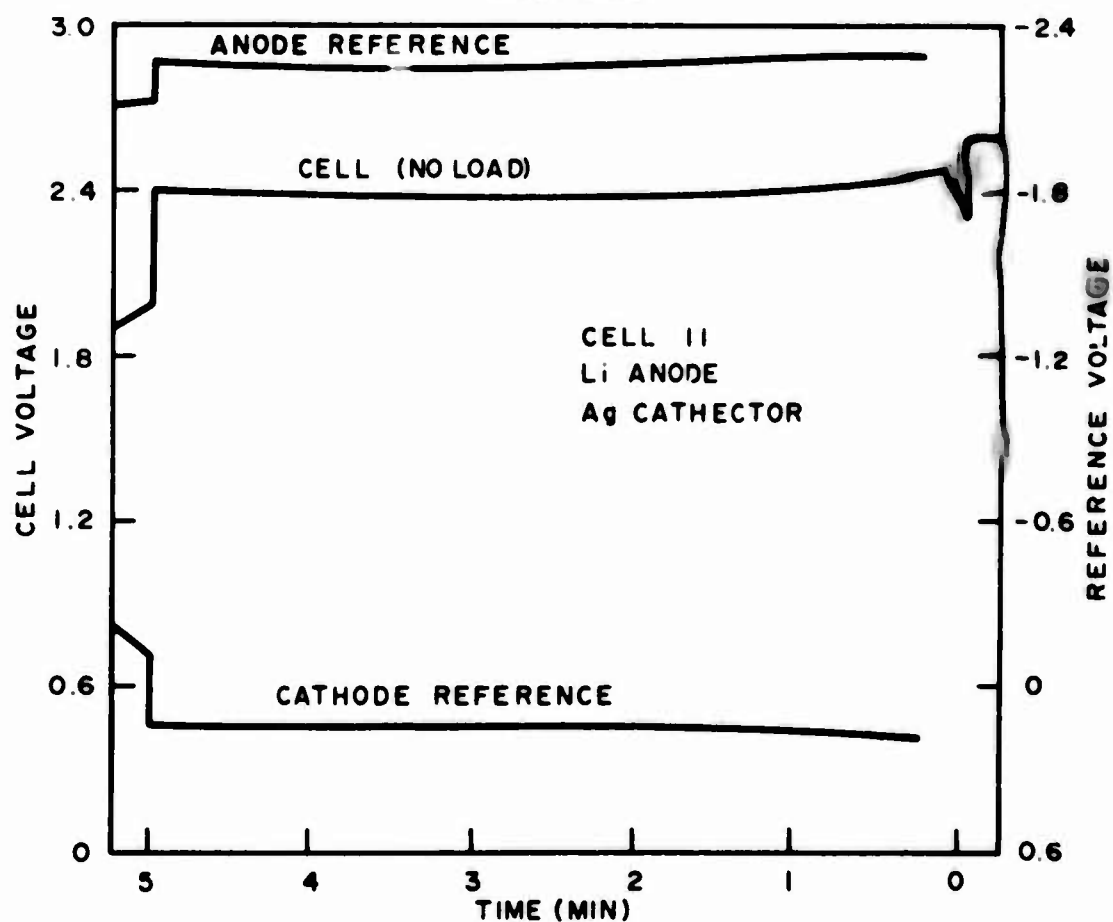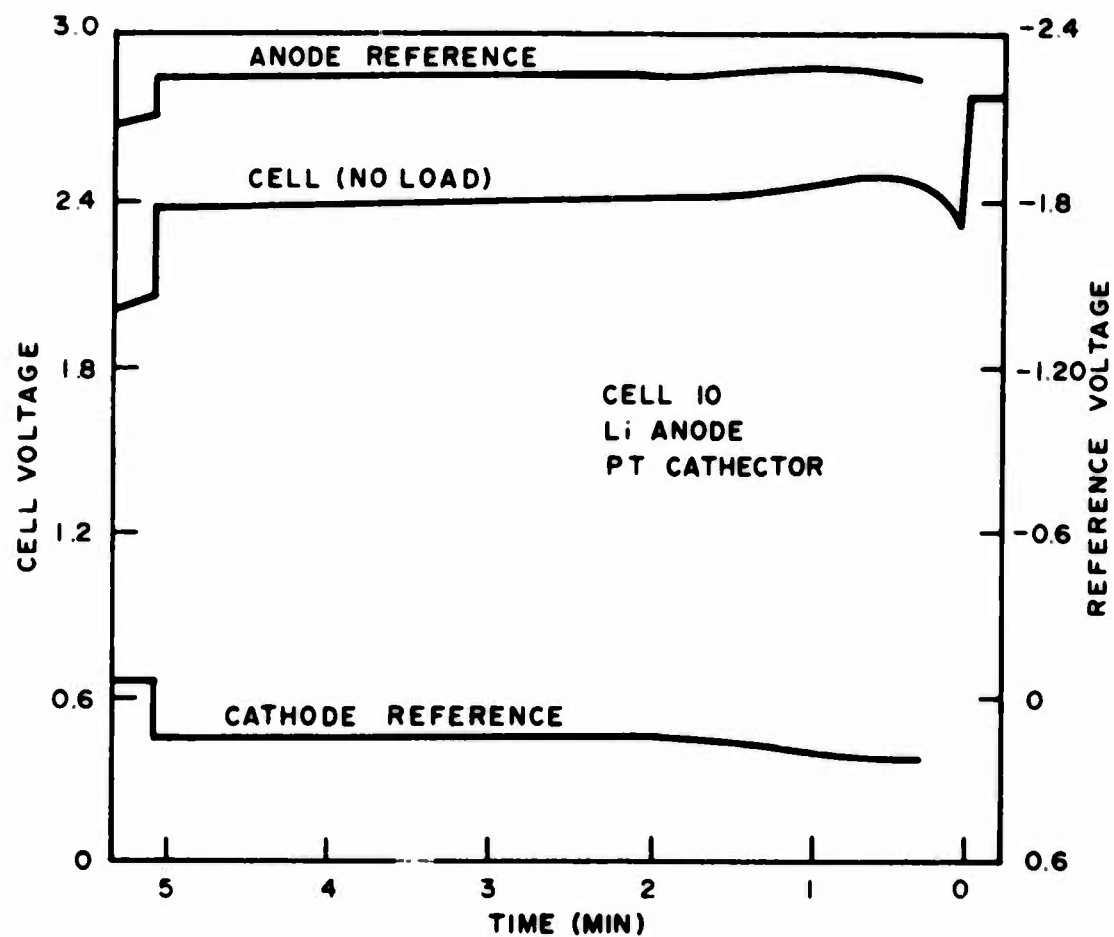
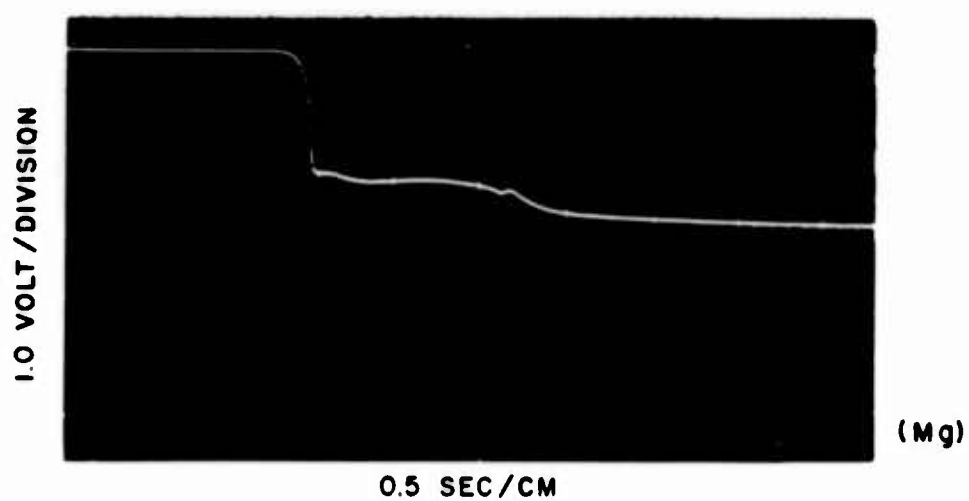FIGURE 17. Experiment 19 Pasted-Cathode Cell
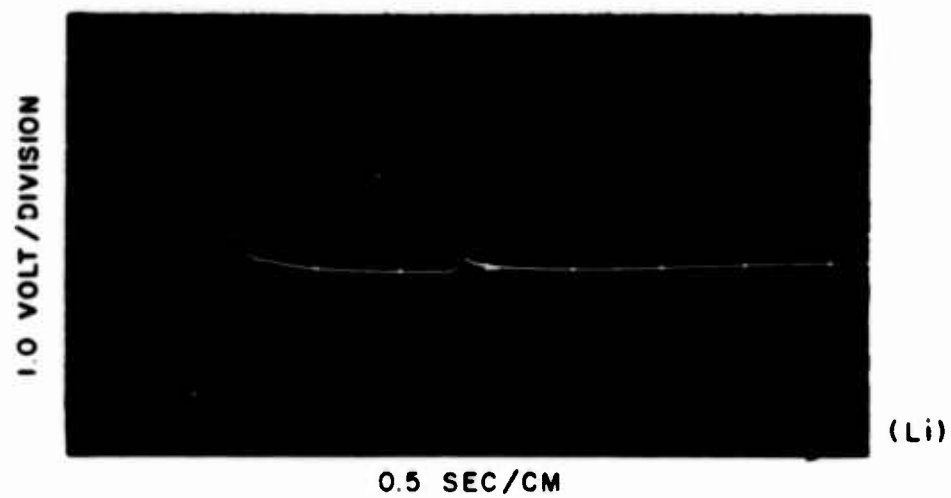Discharge Summary

FIGURE 18. Voltage Rise at Activation
in Experiment 19

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TABLE 5. Experiment-19 Performance Summary
MgR = Rolled Mg bimetal; MgS = sheet Mg

Cell No.	Anode	Cath-ector	Load (ohms)	Cell Voltage at Selected Times						
				Peak	15 Sec	1 Min	2 Min	3 Min	4 Min	5 Min
1	Li	SS	252	2.50	2.25	2.21	2.17	2.16	2.21	2.19
2	Li	Ag	51	2.32	2.15	2.10	2.06	2.04	2.00	1.92
3	Li	Pt	NL	2.46	2.34	2.34	2.34	2.33	2.32	2.34
4	Mg R	SS	NL	1.66	1.64	1.29	1.04	0.94	0.90	0.83
5	Mg R	Ag	201	1.78	1.73	1.49	1.41	1.31	1.27	1.22
6	Mg R	Pt	41	1.59	1.35	1.05	0.83	0.67	0.74	0.57
7	Mg S	SS	41	2.04	1.81	1.45	1.25	1.03	0.90	0.74
8	Mg S	Ag	NL	1.87	1.84	1.49	1.35	1.30	1.34	1.34
9	Mg S	Pt	201	1.81	1.57	1.32	1.17	1.09	1.11	1.10
10[a]	Li	Pt	NL	2.45	2.43	2.41	2.40	2.39	2.39	2.38
11[a]	Li	Ag	NL	2.48	2.45	2.45	2.40	2.39	2.38	2.37

[a]Not part of Latin-square plan.

Conclusions. Experiment 19 led to the following conclusions:

1. The presence of voltage irregularities on all the tests comprising the Latin-square design of this experiment greatly reduced the confidence with which conclusions could be made. In general, it appeared that the choice of cathector material did not significantly affect cell voltages and especially did not account for the disagreement between noload voltages obtained by Harris and those measured in the Mod. 1 cell-test fixture.

2. The performance of the pure sheet Mg anode cells is approximately 10% better than that of the rolled Mg material.

3. It appears that the use of Agfib in cells contributes to cell shorting from within. It is postulated that dendrites of silver form on the surface of the anode and extend into the anolyte pad, eventually shorting to the cathode. Silver is soluble in NH_3 in the presence of an oxidant.

4. Based on tests of cells 10 and 11, the Li anode appears stable on noload.

5. The performance of the $Pb/PbCl_2$ reference electrode is promising, but more evaluation is necessary.

Future Work

Ammonia cell exploratory development will continue in the future along the following lines:

1. The assembling of active materials in an oxygen-free atmosphere will be attempted to determine the effect on cell performance.

2. Work will continue with regard to optimization of active material quantities to match performance specifications.

3. Analysis methods and data retrieval techniques will be improved.

4. Solution activation will be investigated.

5. The use of reference electrodes will continue with sustained attention to providing accurate, stable measurements.

6. The evaluation of Agfib will continue.

7. New cell geometries and materials will be evaluated.

References

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2. Naval Ordnance Laboratory Corona. Quarterly Report: Chemoelectric Energy Conversion for Nonaqueous Reserve Battery Systems, July-September 1963. Corona, California, NOLC, 15 October 1963, NAVWEPS Report 8172. P. 12.

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ANALYSIS AND EVALUATION OF CELL DATA

by

W. C. Spindler

Measurement Error

Experimental error estimates in some of our factorial cell studies have been of the same magnitude as instrument uncertainties. We try to achieve a ±1% standard for instrumentation, but scaling and other factors often introduce uncertainties exceeding ±2%. Since we must develop cells having performance within ±10% limits over all conditions of discharge environment and time, it is necessary to question the adequacy of measurements that may have uncertainties as high as 20% of the allowable cell performance range.

Instrument and reading errors can be separated from product variability according to a procedure described by Grubbs (Ref. 1). Following his example, we connected three Varian recorder channels in parallel to obtain three simultaneous charts of the voltage/time discharge performance of cells in experiment 16, which is discussed in the section of this report on Ammonia Cell Exploratory Development.

All charts were calibrated at 2.20 volts full scale. A dual-channel Varian G22 recorder, rated at ±2% uncertainty, was used for the first and second channels; and a Varian G11 recorder, rated ±1%, was used for the third channel. A response check with a Leeds and Northrup K-3 potentiometer showed less than ±0.02 volt deviation (which is less than ±1% of full scale) across the scale of all three channels. Reading uncertainty was estimated to be constant at ±0.2 division of the charts, which were 12 cm wide and ruled in 100 divisions. In this experiment, reader error proved to be negligible. With a time base of approximately 10 cm/min, the 5-min discharge could easily be read to ±1 mm or ±0.6 sec.

Precision was evaluated at four standard voltage check points: PLV, V10, V30 and V50 (peak load voltage and voltage after 1.0, 3.0 and 5.0 min. of discharge). For the eight cells tested, maximum differences among each set of 24 direct readings at each of these points were, respectively, 1.8, 1.7, 1.3, 1.5 divisions (or 0.04, 0.04, 0.03, 0.03 volt). The standard deviations for precision of measurement determined by Grubb's method are summarized in Table 1. The data for total variability in the second column were obtained by taking the square root of the average of the mean squares for all effects as determined in the analysis of variance of the factorial experiment. This step is justified by the lack of consistently significant effects among the variable factors.

The measurement component of error was less than 10% of total experiment variability in all instances. Precision was poorest at PLV, which reflects the fact that there were substantial differences in the shapes of the voltage curves immediately after activation. Measurement error also was less than 10% (except at PLV) of the 50-mv level previously noted to be about a minimum for the error standard deviation in our factorial experiments.

TABLE 1. Comparison of Measurement Precision
with Total Experiment Variability

Data are from Experiment 16.

Voltage Check Point	Standard Deviation (mv)			
	Total Variability[a]	Meas. Comparison		
		G22R	G22B	G11
PLV	220	6.1	11.	8.2
V10	92	4.7	3.6	0
V30	84	2.2	1.6	2.1
V50	110	3.2	1.6	4.0

[a]Square oot of the average of the mean squares for all effects as determined in the analysis of variance of the factorial experiment.

Since there is an order of magnitude difference between total experiment variability and the component of error due to measurement, it appears that quality recorders of 1 or 2% uncertainty and our general test methods are adequate for present purposes. This conclusion cannot be final, however, because it is based on an analysis that has been concerned with only a small part of a complex instrumentation problem.

For example, there is need for establishing a relationship between the standard deviations in Table 1 and the recorder uncertainty percentage rating. One would like to assert that ±2% of the 2.20-volt full-scale calibration (±0.044 volt) yields a standard deviation that is some fraction of ±0.044 volt. If ±0.044 volt as a limit of error were assumed to be ±3 σ (Ref. 2), then the instrument standard deviation (σ = 15 mv) could be compared directly and favorably with the results in Table 1.

A second important need is to be able to determine the absolute error, rather than just the precision of measurement, in order to be able to compare data obtained from other test groups. These problems can be solved, but present requirements do not justify further effort. These studies will be resumed in the future as needed.

Voltage, Power, and Energy Relations in Single-Cell Performance

The performance of Li/2,4DNA cells in experiment 14 reported last quarter (Ref. 3) was studied further in an effort to determine the relative importance of voltage, power, and energy factors throughout the discharge period. The data for achieved levels in Figure 1 apply to cell 12 (Ref. 3), which was discharged at a fixed load of 16 ohms. Peak load voltage was 2.1 volts, and decay was linear to 1.2 volts after 5 min of discharge. Cell area was 1 cm^2 at the cathode; thus peak cursity was 130 ma/cm^2.

In Figure 1, the achieved levels represent actual cell performance, the specified levels refer to specifications for our FC-2 experimental-model power battery, and the theoretical limits represent cell output that would have been obtained at constant voltage and current. Cell performance compared most favorably with specifications in energy levels and least favorably in power levels.

Energy and Power Efficiencies.
When high energy efficiency is an important requirement for cell performance, low cell voltage may be tolerable. Cell polarization within present limits of experience does not seem to degrade energy yield as much as might be expected. Current, or rate of reaction, appears to be the most important factor, as illustrated in Figure 2. Circled numbers in the table of energies in Figure 2 reference the respective curves. These calculations assume an identical cell of fixed composition, weight, and volume, with only the output assumed different. The actual performance of the Li/2,4DNA cell was similar to curve 7. Curve 1 represents a hypothetical discharge of the same cell at the same current but at maximum obtainable voltage and no decay. This is equivalent to building a cell with only enough reactants to discharge for the required time with 100% efficiency and no polarization. Energy delivered by the actual cell was approximately 50% of this limit.

The table in Figure 2 includes a column for energies that would be obtained if the current were doubled. There is an obvious implication of equivalent performance from the two cases in the upper left and lower right corners; that is, constant high voltage with low current and 40% voltage drop from low initial voltage with high current. However, performance must also be rated according to weight or volume of the cell, which are not included in these data.
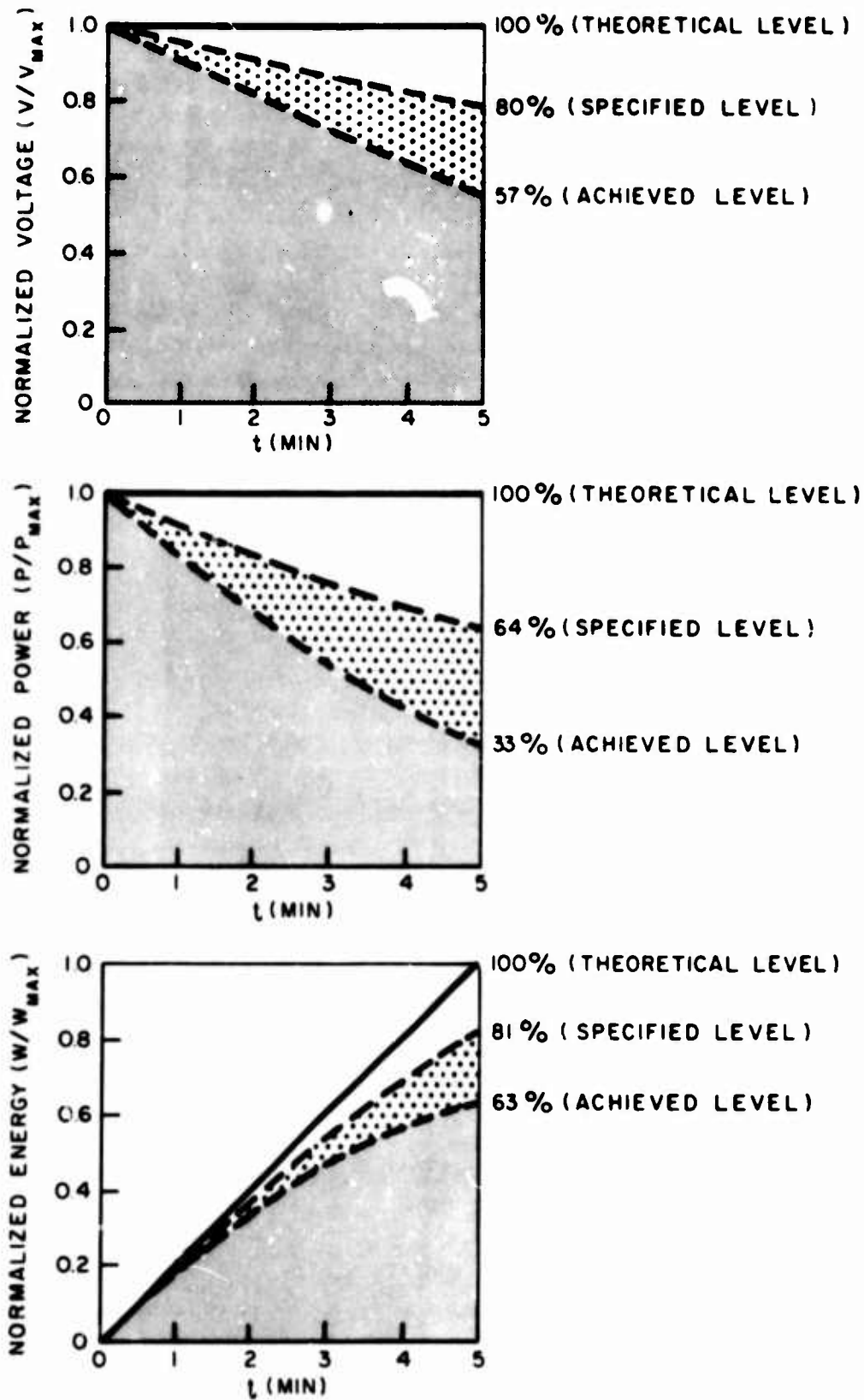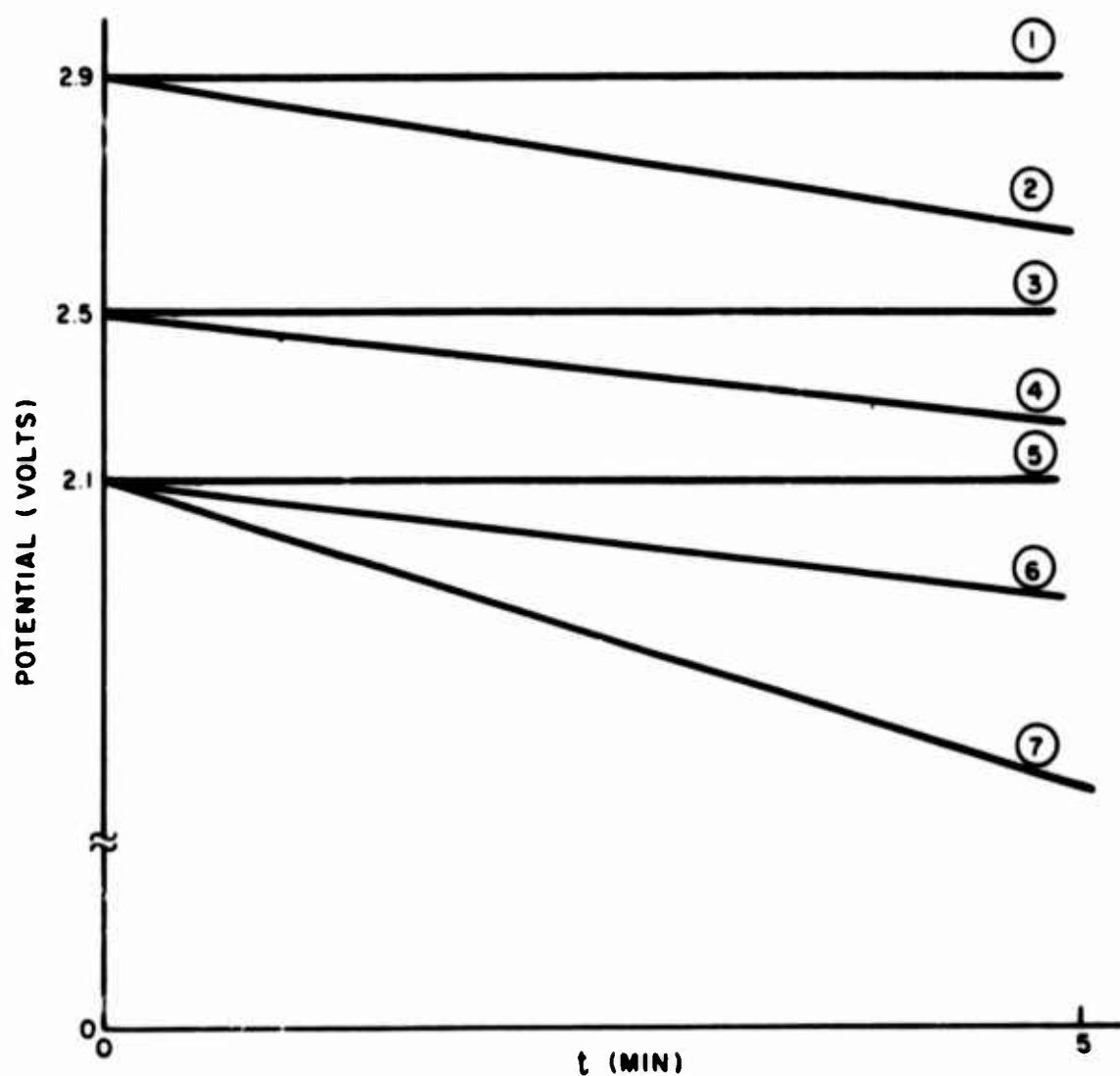
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FIGURE 1. Comparison of Voltage, Power, and Energy Levels at Achieved, Specified, and Theoretical Limits for a Li/2, 4DNA Cell Test

Starting Potential (volts)	Fixed Load (ohms)	Energy (joules) Obtained in 5-min Discharge			
		0 ΔV	20% ΔV	40% ΔV	40% ΔV[a]
2.9	29	87 ①	70 ②	57	114
2.5	25	75 ③	61 ④	49	98
2.1	21	63 ⑤	51 ⑥	41 ⑦	82

[a] Load resistance was $\frac{1}{2}$ listed value in column 2.

FIGURE 2. Calculated Energy Delivered at Different Currents and Voltage Profiles

The interrelationship of energy variables (V, I, t) may be clarified by the pyramid shown in Figure 3. The V_O, I_O base plane represents initial power. Cell discharge proceeds in time along the vertical axis to yield energy. Under fixed load and with cell voltage decreasing linearly with time, energy transfer begins at a maximum rate (P_O), then steadily decreases as cell discharge proceeds.
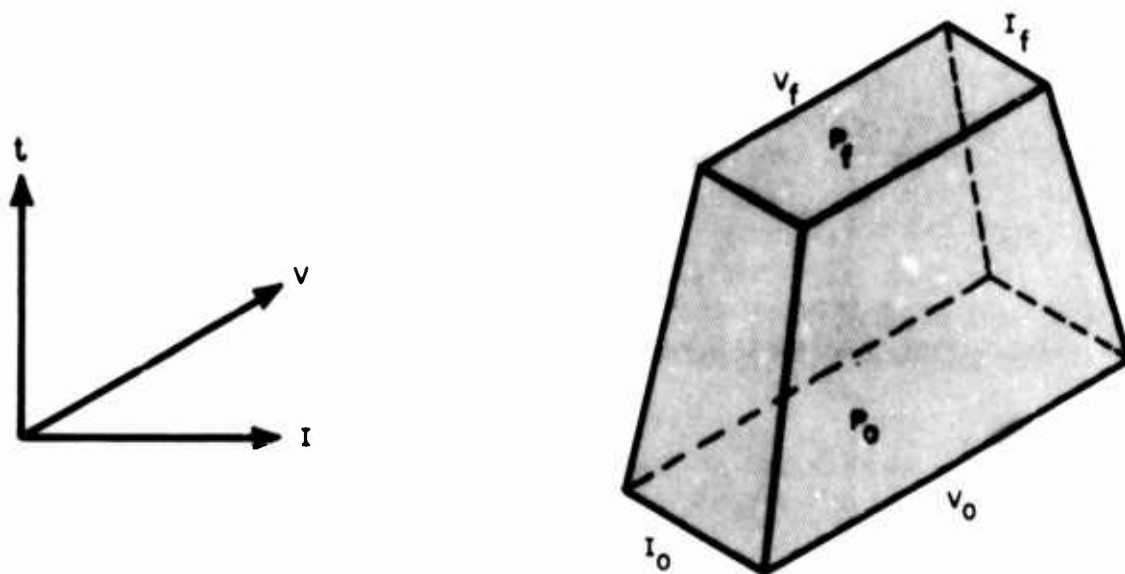

FIGURE 3. Energy Pyramid (W = VIt)

When power regulation is more critical than energy conversion efficiency, the cell reaction rate I is usually reduced. Under fixed load discharge, the slopes of both the V/t and I/t curves diminish, which can be seen in Figure 4 to extend the apex, making the pyramid more like a prism. While this change may appear to improve energy efficiency, the effect is the opposite, since a large amount of unreacted material remains in the cell.

Specifications on batteries nearly always define permissible voltage limits, but it is not always evident whether the battery user is more concerned with power or energy efficiency. For example, our own model FC-2 ammonia battery has ±10% voltage tolerance, but power efficiency is more important. Perhaps the most common example of uncertain treatment of battery factors lies in the nearly universal rating and comparison of batteries by their energy densities (whr/weight or volume), regardless of many obvious variations among the multitude of special purpose designs. Battery development efforts undoubtedly would benefit from more accurate definition of critical parameters for the intended applications.

Cell-Energy Conversion. Cell-energy conversion is frequently calculated from the load R and an average voltage estimated from the V/t discharge curve, using the simplified equation $W = V_{av}^2 \, t/R$. In the above studies of the performance of a Li/2,4DNA cell in Experiment 14, we
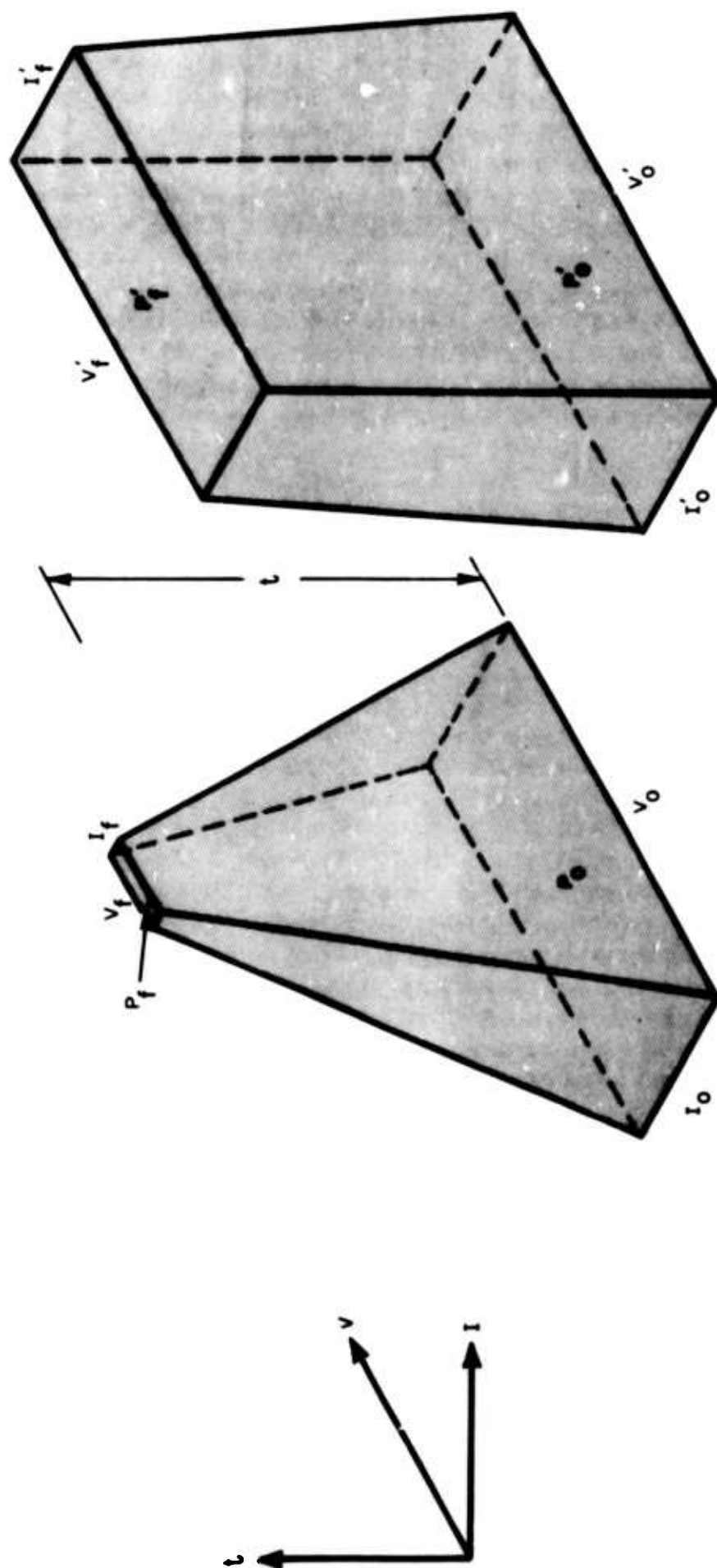
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LOW ΔV
LOW EFFICIENCY

HIGH ΔV
HIGH EFFICIENCY

FIGURE 4.   Differences in Energy Pyramids for High ΔV and Low ΔV

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calculated cell energy both from the average voltage and from the exact, integral equation. Results were unexpectedly similar over the entire range of usable cell performance. Algebraic analysis gave interesting and unique relations. Basic equations have been numbered and appear as a glossary at the end of this article.[1] Equations 7 and 8 show that the difference in energy calculated by the integral and average methods lies solely in the factor 1/3 or 1/4. This slight change of constant influences a t^3 term, which affects energy calculation only near the end of discharge.

Selected values are given in Table 2, based on performance of the Li/2, 4DNA cell discharged into a fixed 16-ohm load. Energy calculated from average voltage is low by only $\frac{1}{2}$% of true value when the cell has discharged to 0.8 PLV, low by $3\frac{1}{2}$% at 0.5 PLV, and only $7\frac{1}{2}$% low when cell voltage has dropped to 0.33 PLV. The maximum difference of 25% (ratio of 1/4 to 1/3) occurs at zero voltage. At end of the discharge period, $V = O$, $t = b/a$, and $V_{av} = b/2$. Total energies are

$$W_{av} = \frac{b^3}{4aR} \qquad \text{(using } V_{av}\text{)}$$

$$W_{in} = \frac{b^3}{3aR} \qquad \text{(by integration)}$$

$$W_{av}/W_{in} = 3/4$$

There is a special significance in Table 2 for the line entry at time

TABLE 2. Comparison of Cell-Energy Conversions Calculated
From Average and Integral Voltage Functions
R = 16 ohms; V = 2.1 - 0.18t

Time (min)	Potential		Power (watts)	Energy			
	volts	%PLV		Integral (joules)	Average (joules)	$\frac{\text{Average}}{\text{Integral}}$	Percent of Total
0	2.10	--	0.27	0	0	-	-
b/5a	1.68	80	0.18	51	51	0.995	80
b/2a	1.05	50	0.07	56	54	0.965	87
2b/3a	0.7	33	0.03	62	57	0.925	97
b/a	0	0	0	64	48	0.750	100

---

[1] These equations were derived for the special case of (1) discharge into fixed load and (2) linear voltage decline.

2b/3a. At this point, average power calculated from Equation (6) or (8) is zero, and it is negative thereafter to final time at V = O. Thus W_{av} (average energy) is maximum at t = 2b/3a and then begins to diverge rapidly from W_{in} (integral energy) as t → b/a. The energy equations at this inflection point are

$$W_{av} = \frac{8b^3}{27aR}$$

$$W_{in} = \frac{26b^3}{81aR}$$

$$W_{av}/W_{in} = \frac{12}{13} = 0.925$$

This is a remarkably small difference for a cell discharge that has proceeded through 2/3 of its time limit and 97% of its total energy yield. The use of average voltage to simplify energy calculations seems clearly justified, provided the limitations imposed by this analysis are recognized.

Another pertinent relation concerns the total integrated energy equation. In Equation 7, substituting the end time expressed by the constants in the voltage equation, b/a, the total energy is

$$W_{tot} = \frac{1}{3} \frac{b^3}{aR}$$

This equation represents the volume of a pyramid, which can be drawn with base VI and altitude t, where VIt = $b^3/(aR)$, as shown in Figure 4. Increased energy can be obtained by increasing peak voltage b, or current b/R, or time b/a; or by decreasing slope 1/a. It must be kept in mind that these results apply only to the linear decay curve and not to any kind of plateau decay curve.

The battery engineer may find considerable interest in the Table 2 data, which show that during the first 20% of the voltage decay period, 80% of the total energy is delivered. Extending cell discharge time to 50% voltage drop increases energy yield only 7% to 87%. This result tends to contradict a common point of view that to obtain high energy efficiency an appreciable voltage drop is to be expected.

Glossary of Terms and Equations

P   Power in watts
R   Resistance in ohms
V   Cell potential in volts
W   Energy in joules
a   Slope of V/t curve in volts/min
b   Initial cell potential in volts
t   Time in min

$$V = b - at \qquad\qquad \text{potential} \qquad\qquad (1)$$

$$P = \frac{V^2}{R} \qquad\qquad \text{power} \qquad\qquad (2)$$

$$W = \frac{V^2 t}{R} \qquad\qquad \text{energy} \qquad\qquad (3)$$

$$\frac{dV}{dt} = -a \qquad\qquad \text{potential slope} \qquad\qquad (4)$$

$$\frac{dP}{dt} = \frac{-2aV}{R} \qquad\qquad \text{power slope} \qquad\qquad (5)$$

$$\frac{dW}{dt} = \frac{V^2}{R} \qquad\qquad \text{energy slope (power)} \qquad\qquad (6)$$

$$W_{in} = \frac{1}{R} \int_{o}^{t} V^2 \, dt$$

$$= \frac{tb^2}{R}\left(1 - C_1 + \frac{C_1^2}{3}\right) \qquad \text{energy (by integration)} \qquad\qquad (7)$$

where

$$C_1 = \frac{at}{b}$$

$$W_{av} = \frac{V_{av}^2 \, t}{R}$$

$$= \frac{tb^2}{R}\left(1 - C_1 + \frac{C_1^2}{4}\right) \qquad \text{energy (from av. potential)} \qquad\qquad (8)$$

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